ELECTRON TRANSPORT DYNAMICS IN ROOM TEMPERATURE
REDOX MOLTEN SALTS AND CHEMISTRY OF MONOLAYER-
PROTECTED AU NANOPARTICLES

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ABSTRACT

WEI WANG: Electron Transport Dynamics In Room Temperature Redox Molten Salts And Chemistry of Monolayer-Protected Au Nanoparticles
(Under the direction of Royce W. Murray)

Chapter One briefly introduces the basics of redox molten salts and monolayer-protected Au nanoparticles.

Chapter Two examines the mass transport of counterions in molten salts of ruthenium complexes where the counterions are mixtures of perchlorate and iodide ions. The average diffusion coefficients of the counterions were obtained by ionic conductivity impedance measurements, while that of iodide (as a surrogate for perchlorate ion transport) was measured directly using iodide voltammetry. Agreement between the conductivity-based and Faradaic counter ion transport data provides a quantitative validation of previous use of ionic conductivity data in electron transfer dynamics study in redox semi-solids.

Chapter Three focuses on the ligand-exchange reaction of phenylethanethiolate (SC2Ph) ligands on 1.1 nm Au nanoparticles with varied amounts of triphenylphosphine. The results from UV-Vis, NMR and electrochemistry suggest that the reaction liberate Au^1SC2Ph complexes (accompanying core size change), as opposed to SC2Ph thiols, the common out-coming ligands in thiolat-to-thiolate ligand exchange reaction on Au nanoparticles.
Chapter Four explores a room-temperature Au$_{38}$ nanoparticle polyether melt in which voltammetric and chronoamperometric, and impedance measurements have been made, respectively, of the rates of electron and ion transport in the melt. The measured rates of electron and of electrolyte ion transport are very similar, as are their thermal activation energy barriers, observations that are consistent with a recently introduced ionic atmosphere relaxation model for control of electron transfer in redox polyethers.

Chapter Five describes ferrocenated imidazolium molten phases where ferrocene is chemically linked to various dialkylimidazoliums. The physical properties, including density, fluidity, and ionic characteristics, are discussed. The electrochemical results are presented in Chapter Six. It is observed that the electron diffusion in structurally-different ferrocenated imidazoliums is more efficient than the physical transport of redox ions. The rate of electron transfer is linearly correlated to the counterion diffusion, the first observation from imidazolium-based redox semi-solids consistent with the counterion relaxation control of electron transfer model.

Chapter Seven investigates the surface properties of Au nanoparticle films contacted with imidazolium ionic liquids. A dynamic contact angle change is observed and explained on the basis of anion penetration which is further compared to the formally similar electrowetting phenomenon.
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<tr>
<td>bpy</td>
<td>bypridine</td>
</tr>
<tr>
<td>C</td>
<td>concentration</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>C6</td>
<td>hexanethiolate</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>interfacial tension</td>
</tr>
<tr>
<td>$d$</td>
<td>density</td>
</tr>
<tr>
<td>$D_{\text{APP}}$</td>
<td>apparent diffusion coefficient</td>
</tr>
<tr>
<td>$D_{\text{CION}}$</td>
<td>physical diffusion coefficient of counterions</td>
</tr>
<tr>
<td>$D_{\text{E}}$</td>
<td>electron diffusion coefficient</td>
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<tr>
<td>$D_{\text{ION}}$</td>
<td>physical diffusion coefficient of ions</td>
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<tr>
<td>$D_{\text{PHYS}}$</td>
<td>physical diffusion coefficient of redox species</td>
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<td>DPV</td>
<td>differential pulse voltammetry</td>
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<tr>
<td>$\delta$</td>
<td>average center-to-center distance of redox sites</td>
</tr>
<tr>
<td>$E$</td>
<td>potential</td>
</tr>
<tr>
<td>$E_A$</td>
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<tr>
<td>$\Delta E_p$</td>
<td>peak potential difference</td>
</tr>
<tr>
<td>$e$</td>
<td>electric charge of an electron or elementary charge</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>dielectric constant</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>Fc</td>
<td>ferrocene</td>
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<tr>
<td>FFV</td>
<td>fractional free volume</td>
</tr>
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<td>$\Delta G^\ddagger$</td>
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\( \eta \) viscosity
\( \theta \) contact angle
Im imidazolium
\( i_{p,a} \) anodic peak current
\( i_{p,c} \) cathodic peak current
\( \kappa \) electronic transmission coefficient
\( k^o \) heterogeneous electron transfer rate constant
\( k_B \) Boltzmann constant
\( k_{EX} \) rate constant for electron-self exchange reaction or electron transfer reaction
\( K_p \) donor-acceptor precursor complex formation constant
MePEG poly(ethylene) glycol methyl ether
MePPG poly(propylene) glycol methyl ether
\( v_n \) nuclear frequency factor
PEG poly(ethylene) glycol
PhC2 benzeneethanethiolate
PPG poly(propylene) glycol
QRE quasi-reference electrode
\( r \) hydrodynamic radius
\( R \) molar gas constant
\( \sigma \) ionic conductivity or surface excess charge
\( t \) time or transference number
\( T \) temperature
\( T_g \) glass transition temperature
$\tau_L$  longitudinal relaxation time
$
u$  potential scan rate
$V$  electric potential
$z$  ionic charge
CHAPTER I

BASICS OF ROOM TEMPERATURE REDOX MOLTEN SALTS AND MONOLAYER-PROTECTED AU NANOPARTICLES

1.1 Introduction

Organic molten salts with melting point at room temperature or lower, or so-called ionic liquids in modern vocabulary, have been known for years dated from early 1910s when the alkylammonium nitrate was first reported.\(^1\) Since the late 1970s, room temperature molten salts, mainly haloaluminated alkylpyridinium or 1,3-dialkylimidazolium type, have gained more attention in a variety of commercial applications such as batteries, metal deposition, and capacitors.\(^2\) Nonetheless, the promise of ionic liquids was hurt by the fact that the aluminium halide was sensitive to moisture. This challenge was soon overcome by the emergence of air- and moisture-stable ionic liquids where haloaluminate was replaced by water-stable anions such as tetrafluoroborate and hexafluorophosphate, first reported in 1992.\(^3\) Over the last decade, the ionic liquid has been very popular in a broad range of scientific disciplines such as organic synthesis,\(^4\) catalysis,\(^5\) separation,\(^6\) photochemistry\(^7\) and, more dominantly, electrochemistry.\(^8\) It is widely proposed that the ionic liquid is a promising alternative to conventional solvent thanks to their unique physical and chemical properties including negligible vapor pressure, low toxicity, high chemical and thermal stability,
intrinsic ionic conductivity, significantly large electrochemical potential window and capability of dissolving a variety of organic and inorganic compounds.\textsuperscript{9}

While most electrochemical-related studies involve ionic liquid as simply a solvent where redox compound dissolves, a novel type of electro-active room temperature molten salts was initially developed and systematically explored by Murray and coworkers with the basic idea of covalently combining low melting point polymer electrolyte\textsuperscript{10} or dialkylimidazolium\textsuperscript{11} with redox compounds. The resulting material\textsuperscript{5}, while maintaining most advantages intrinsic to normal ionic liquids, offer an unusual high concentration of redox sites (as high as 3 M)\textsuperscript{11} and work as ideal media for the study of homogeneous electron transfer dynamics. Our interest in the electron transport mechanism is propelled by the potential application of redox ionic liquid in the areas of energy storage\textsuperscript{12} and molecular electronics.\textsuperscript{13} The primary goal is aimed to elucidate the fundamental structure-property relationship and the crucial environmental factors determining the electron transport rate. A comprehensive knowledge in this matter is of importance and required in the rationally design of redox ionic liquid system for eventual practical applications.

Among various redox moieties explored is there a special category which is primarily composed of tens to hundreds of Au atoms with the protection of a monolayer of organic ligands, namely, monolayer-protected Au nanoparticles.\textsuperscript{14} With core diameter in the regime of sub-nanometer, the properties of Au nanoparticles bridge bulk metal and molecular metal complexes and are strongly dependent on the core size.\textsuperscript{15} The magic of monolayer-protected Au nanoparticles is further played with the monolayer functionalization which leads to a variety of nanoparticles for different purposes including studies of homogeneous electron transfer and interfacial phenomena, as described in following chapters.
1.2 Hybrid Redox Polyethers

1.2.1 Structure, Physical Properties and Experimental Setup

The most widely explored strategy of forming redox molten salts in Murray’s lab is to chemically attach poly(ethylene) glycol (PEG) to redox compounds. The resulting hybrid redox polyethers, while fluid enough to maintain liquid-like amorphous state at room temperature, have a high concentration of redox sites. Some illustrative examples are shown in Figure 1.1. The PEG-attached redox ions can be combined with a variety of counterions. In a very unique case, cobalt(tribipyridine) complex cations associate with phosphate anions of DNA, forming so-called liquid DNA. As a matter of fact, the route to the hybrid redox polyethers is so general that not only can the PEG be linked with redox ions, it can be also attached to their counterions. This has been a powerful approach to prepare redox ionic liquid in that essentially all redox ions, including those not amenable to covalent attachment, can be made into a molten phase by simple ionic association with PEG-tailed counterions. A few examples of this genre are shown in Figure 1.2. The strategy of forming redox ionic liquid is also applicable to neutral redox compounds where the covalent attachment of PEG results in molecular melts. An added electrolyte (e.g. LiClO₄) renders the material ionically conductive and makes the voltammetric measurements possible. Representative examples of this category include ferrocene (Fc), tetrathiafulvalene (TTF), porphyrin and even Au nanoparticles, as illustrated in Figure 1.3.

The inclusion of PEG in the molecular structure has a substantial effect on crystallinity of material. For example, the viscosity of material strongly depends on the length of PEG chains and amount of PEG component involved. The initial effort to couple PEG with molecular weight of 2590 with ferrocene carboxylate resulted in a waxy solid at
Figure 1.1 Structures of hybrid redox polyethers, where n is the average number of ethylene oxide unit in the polymer chain. (A) Viologen(MePEG)$_2$ $^{16a}$ (B) Metal tris(4,4’-dicarboxy-MePEG-2,2’-bipyridine) complexes coupled with anions of DNA $^{16b}$, sulfonated polystyrene $^{16c}$, and perchlorate $^{17}$ (C) Cobalt tris(4,4’-dicarboxy-polypropylene oxide-2,2’-bipyridine) perchlorate complex $^{18}$. 
A. $M=\text{Fe, Co, Ru, Os, Cu, Ni}$

B. $n=3, 7, 12, 17$

C. $n=1, 2, 3$
Figure 1.2 Structures of hybrid redox polyethers with (A) MePEG$_{350}$ triethyl ammonium cations coupled with anions of (from left to right) anthraquinone-2-sulfonate $^{19a}$, hexacyanoferrate $^{19b}$, and metal tris(bathophenanthroline disulfonate) $^{19a}$, (B) MePEG$_{350}$ sulfonate anions coupled with cations of cobaltocene $^{20a}$, pyrazine bridged binuclear pentaammine ruthenium $^{20b}$ and ferrocenylmethyltrimethylammonium $^{20a}$, and (C) MePEG$_{350}$ benzene sulfonate anions coupled with cations of hexaammine ruthenium and metal tris(bipyridine) $^{19a}$. 
A. \( \text{Co}^+ \)  

\[ \text{Ru(NH}_3)_6^{3+} \]

B. \( \text{Fe}(\text{CN})_6^{3-} \)

\[ M = \text{Fe, Co, Ru} \]

C. \( \text{Ru(NH}_3)_6^{3+} \)

\[ M = \text{Ru, Co} \]
room temperature which became an amorphous melt only when heated up to 60°C.\textsuperscript{10a} It was later determined that employing shorter PEG with molecular weight of 550 or less greatly improved the fluidity of material which was liquid-like at room temperature.\textsuperscript{17} Even with the same length of PEG chain, the viscosity of material is different with varied amount of PEG present. For example, ruthenium(trisbipyridine) complex linked with two PEG chains (MW=350) has the viscosity of 8.7\times10^6 \text{cP} at 25°C, which is two orders of magnitude more viscous than the same complex with six attached PEG chains ($\eta=4.4\times10^4 \text{cP}$).\textsuperscript{22} The fluidity of redox molten salts can be also manipulated by extra free PEG\textsuperscript{23a} added as a plasticizer, or by sorption of high pressure CO$_2$ gas\textsuperscript{23b}.

The viscosity of redox molten salts is an important consideration in electrochemical studies due to its strong effect on the rate of ionic mass transport. Despite an abundance of charge carriers, the ionic conductivity of molten salts is only modest ($10^{-5}$-\text{to}-$10^{-7}$ S cm$^{-1}$) due to the fairly slow rate of ionic mobility constrained by the insufficiently-solvated, viscous environment. The low conductivity of molten salts makes conventional voltammetry, where a macroelectrode (surface area ~ mm$^2$) is used and the current is on µA scale, rather difficult due to the significant $iR_{\text{UNC}}$ distortion. However, this challenge is bypassed by the use of ultramicroelectrodes with diameter of 25 µm or smaller.\textsuperscript{24} The diminished electrode surface restricts the current to the nA to pA scale and minimizes the $iR_{\text{UNC}}$ effect to an acceptable level. The $iR_{\text{UNC}}$ effect can be further reduced by monitoring the redox chemistry in a timescale slower than the traditional dilute solution electrochemistry. For example, the cyclic voltammograms are obtained with potential scan rates ranging from 20 mV/s to as slow as 50 µV/s. What should be mentioned is that, although the ultramicroelectrode and slow scan rate are employed, the cyclic voltammogram of redox molten salts is still typically in the regime
Figure 1.3 Structures of hybrid redox polyethers where redox species is at neutral charge state. (A) Ferrocene(CO$_2$MePEG)$_2^{21a}$ (B) Tetrathiafulvalene(MePEG)$_4^{21b}$ (C) Tetra(phenyl-MePEG) porphyrin$^{21c}$ (D) Perylene di(MePEG)imide$^{21d}$ (E) Ruthenium dicyano bis(4,4’-dicarboxyMePEG-2,2’-bipyridine)$^{21e}$ (F) MePEG-C6-S thiolate protected Au$_{38}$ nanoparticles (monolayer mixed with benzeneethanethiolate ligands)$^{21f}$
of linear diffusion and the limiting current plateau characteristic of microelectrode voltammetry in dilute solution is not observed. As a matter of fact, the diffusion layer thickness of redox molten salts is usually less than or comparable to the dimension of microelectrode surface used, so that the voltammograms in redox molten salts appear more “conventional”.

A schematic representation of an experimental setup is illustrated in Figure 1.4. A four-electrode assembly, capable of both three-electrode voltammetry and two-electrode conductivity measurement, is made by sealing electrodes in the stainless steel tube with resin epoxy.\textsuperscript{23b} The assembly contains a 25 µm diameter Pt disk microelectrode, a 0.5 mm Ag quasi-reference electrode and two 0.4 mm diameter Pt disk auxiliary electrodes. A drop of ionic liquid sample is cast onto the top of electrode which is eventually moved into a glass chamber under active vacuum and temperature control. The volatile casting solvent and oxygen in the sample is removed by exposing the sample to reduced pressure for prolonged time at elevated temperature (typically, 65–75°C). The small current electrochemistry is carried out with a home-made high gain, low noise potentiostat\textsuperscript{25} which, together with the electrode setup, is placed in a Faraday cage.

\subsection*{1.2.2 Electron Transport Dynamics}

The redox molten salts are unique media for the study of electron transport mechanism in that, while the mass transport of redox species is severely constrained, the unusual high concentration of redox sites facilitates the efficient charge transport through electron self-exchange reactions (electron hopping) between redox sites. A cartoon of electron transport is shown in Figure 1.5. The electrochemical current collected is the
combination of both electron diffusion \((D_E)\), contributed by electron self-exchange reaction \((kEX)\), and physical diffusion \((DPHYS)\), as described by the Dahms-Ruff equation:  

\[
D_{APP} = D_{PHYS} + D_E = D_{PHYS} + \frac{k_{EX} \delta^2 C}{6} 
\]  

(1)

where \(D_{APP}\) is the apparent diffusion coefficient, \(\delta\) is the equilibrium center-to-center distance between electron donor and acceptor, and \(C\) is total redox site concentration in the melts. The right hand term in equation (1) is derived with the assumption of a simple cubic lattice model. In dilute solution where average separation of redox species is significant, the \(D_{APP}\) is dominated by the \(D_{PHYS}\) of redox moieties with negligible \(D_E\). On the contrary, \(D_E\) in redox molten salt is more pronounced while \(D_{PHYS}\) is depressed to a much smaller value.

The meaning of the Dahms-Ruff equation is made clearer with an example of cyclic voltammogram obtained from Co metal complex molten salts, as shown in Figure 1.6.\(^{17b,c}\) The Co(III/II) current on the positive side is small due to the sluggish electron self-exchange reaction with essentially zero electron transfer rate.\(^{27}\) The current of Co(III/II) is therefore only contributed by the physical diffusion of metal complexes. However, the peak of Co(I/II) on the negative region is much larger than that of Co(III/II), reflecting a increased apparent diffusion coefficient. The enhanced \(D_{APP}\) is due to the electron diffusion which is the result of facile electron hopping reaction of Co(I/II). It is clear from the peak current difference that \(D_{PHYS}\) is much smaller than \(D_E\) and \(k_{EX}\) can be calculated from \(D_{APP}\) with ignored \(D_{PHYS}\).

A general observation in electron transfer dynamics study is that the electron self-exchange rate constants in redox molten salts are smaller and the thermal barriers are larger than the same electron donor-acceptor pair in dilute solution.\(^{19a, 21c, 28}\) In the context of modern electron transfer theory, the correlation between electron transfer rate constant and thermal barrier is described as:  

\[\text{rate} = \frac{1}{\exp\left(\frac{\Delta G^*}{kT}\right) + 1}\]
Figure 1.4 Setup for electrochemical measurements on redox molten salts in vacuum.
Melt Sample

Ag QRE

Temp Control

Pt WE1 (d=25 mm)

Pt CE

Vacuum

EP O-ring

Epoxy resin

Steel tube

Melt Sample

Ag QRE

Pt WE1 (d=25 mm)

Pt CE

Pt WE2 (d=0.4 mm)

Epoxy resin

Steel tube
**Figure 1.5** A cartoon of electron and physical diffusion process in redox molten salts.
Electron self-exchange reaction

$D_{\text{PHY}} \ll D_E$

$D_{\text{APP}} = D_{\text{PHYS}} + D_E$

REDOX SITE

Electron self-exchange reaction

$k_{\text{EX}}$
where $K_p$ is the donor-acceptor precursor complex formation constant, $\kappa$ the electronic transmission coefficient, $\nu_n$ the nuclear frequency factor, and $\Delta G$ the activation free energy ($\approx E_{A,EX}$ for symmetrical reaction). While there is no decrease of electronic coupling in the pre-exponential term, the reduced $k_{EX}$ is mainly accounted by the larger thermal barriers.\textsuperscript{17c}

The thermal barriers of electron transfer from the electrochemical measurements, when compared to the out-sphere outer-sphere reorganization barrier energies predicted based on classical Marcus theory, are 3-5 times larger.\textsuperscript{17c} Those thermal barriers are also larger than the barrier values obtained from experiments of optically induced electron transfer in binuclear and mononuclear pentaamine pyridine ruthenium melts.\textsuperscript{20b} Clearly, there is an additional energy contribution to thermally activated electron transport process in redox molten salts.

The earliest analysis\textsuperscript{17b,d,28c,30} of electron transport dynamics in PEG-based molten salts was based on the idea of solvent dynamics control, in which the electron transfer rate constant is inversely proportional to the longitudinal solvent relaxation time (or viscosity) predicted by:\textsuperscript{31}

$$\nu_n = \tau_L^{-1} \left[ \frac{\Delta G_{OS}^*}{4\pi RT} \right]$$ \hspace{1cm} (3)

where $\Delta G_{OS}$ is the out-sphere reorganizational barrier energy, and $\tau_L$ is the longitudinal solvent relaxation time. Given that the physical diffusion of redox species in molten salts is inevitably associated with the repolarization of ether dipoles and polyether chain motion, the electron transfer rate under the context of solvent dynamics control is further related to $D_{PHYS}$.\textsuperscript{17d,31} While the initial data from Co(tribipyridine) and Fc(trisbipyridine) complex
Figure 1.6 Microelectrode (Pt, 25µm dia.) cyclic voltammogram (10 mV/s) of neat undiluted [Co(bpy(CO₂MePEG₃₅₀)₂)₃][ClO₄]₂ molten salt at different temperatures in vacuum.
molten salts did not show conclusive correlation between homogeneous electron transfer rate constant and fluidity,\textsuperscript{17c,22} a remarkable linearity (slope=0.82) over a more than $10^{11}$-fold range between heterogeneous electron transfer rate and physical diffusion coefficient of redox ions was observed in Co complex molten salts with varied PEG length and concentration of electrolyte and free PEG, clearly suggesting a strong solvent dynamics control of heterogeneous electron transfer.\textsuperscript{17d} Further experiments where Co(tribipyridine) and Co(phenanthroline) complex molten salts are plasticized by high pressure CO\textsubscript{2} and free PEG show that there is also a linear correlation between homogeneous electron transfer rate and $D_{\text{PHYS}}$ with slope of 0.7, evidence again suggesting solvent dynamics control of homogeneous electron transfer.\textsuperscript{23b,32}

Although the solvent dynamics control seemed a reasonably good model, a better correlation between electron transfer rate constant and diffusion coefficient of counterions was later recognized with unity slope, for various redox molten salts.\textsuperscript{20a, 21e,f, 32, 33} While the coupling of electron transfer rate with counterion diffusion could be regarded as another form of solvent dynamics control, the result is better interpreted on the basis of ion pairing and rearrangement of the ionic atmosphere during the electron transfer, namely, ion atmosphere relaxation control of electron transfer. Evidence for the coupling of electron transport to counterion mobility extends over a wide range of PEG-based molten salts. For example, for cobalt and ruthenium complex molten salts, the results demonstrate (a) a 1:1 proportionality between counterion diffusion coefficient and both heterogeneous (e.g. Co(III/II))\textsuperscript{23a} and homogeneous (e.g. Co(II/I))\textsuperscript{23b, 32}, Ru(III/II)\textsuperscript{21e, 33}) electron transfer rates, (b) very similar thermal energy barriers for electron transfer and counterion diffusion, and (c) electron transfer rates fall to effectively zero when the counterion (e.g., DNA\textsuperscript{16b}) is immobile.
Substantial effort has been put into structural variations of metal complex molten salts in terms of metals (Co, Ru), counterions (ClO$_4^-$ or I$^-$_3), PEG linkage (to cation or anion)$^{32,23a}$, number of PEG chains $^{21e,33}$, supporting electrolyte addition$^{21e}$ and CO$_2$ plasticization$^{23b,32}$. All of these examples have entailed more or less conventional redox materials, and all have shown adherence to the ionic relaxation analysis. The *generality* of ionic atmosphere relaxation for describing electron transfer in rigid ionic environment is further strengthened by electron transfer study in less conventional redox reactions such as molecule-like Au nanoparticles$^{21f}$. The result again gives linear correlation between $k_{EX}$ and $D_{CION}$ with near unity slope.

The generality of the ion atmosphere relaxation model can be further explored by developing structurally different redox molten salts system which is not solely based on the polyethers. The increasing interest in the dialkylimidazoliums as ionic liquids prompts us to a new synthetic route to redox molten salts where the ferrocene is covalently linked with one alkyl chain of dialkylimidazolium, resulting a so-called ferrocenated imidazolium ionic liquid.$^{11}$ The fluidity of ferrocenated imidazolium spans a wide range of from $10^3$ to $10^7$ cP at room temperature, depending on the specific molecular structure, which can be fine-tuned by varying the length of alkyl groups and coupling to different anions. Preliminary electron and mass transport results in ferrocenated imidazolium ionic liquid show that the correlation between electron transfer rate and ionic diffusion again follows the ion atmosphere relaxation control of electron transfer and is consistent with the observations in various hybrid redox polyethers.$^{11b}$

1.3 *Monolayer-Protected Au Nanoparticles*
1.3.1 Size-dependent Properties

The interest in the redox molten salts extends not only in the direction of exploring different softening organic component but also toward various redox species. A unique one of them is the monolayer-protected Au nanoparticle. With the synthetic route first introduced by Brust et al., a variety of Au nanoparticles with the core diameter discretely ranging from 1.1 nm to 5 nm are synthesized and separated with reasonably good monodispersity. The structure and chemical composition of Au nanoparticles are routinely analyzed by TEM, TGA, NMR, MS, and electrochemistry, giving molecular formula with the average number of core atoms and protecting ligands. Of all the Au nanoparticles studied in Murray’s lab, the two best-studied examples are 1.6 nm Au$^{140}(SC6)_{53}^{35}$ and 1.1 nm Au$^{38}(PhC2)_{24}^{36}$.

The electronic and optical properties of Au nanoparticles are strongly dependent on the size of metal core. The molecule-like properties such as discrete electronic states start to emerge when the particles are made smaller and the bulk metallic band energetics yield to quantum confinement effects. A comparison of optical absorbance spectra and electrochemistry for Au nanoparticles with different core size is shown in Figure 1.7. While larger Au nanoparticles are more similar to bulky metal and show featureless voltammogram and absorbance spectra (with surface plasmon band around 520 nm), the electrochemistry for smaller size Au$^{140}$ shows evenly spaced oxidation and reduction peaks, a single electron transfer behavior named quantized double layer charging. The peak spacing ($\Delta V$) is related to the single electron charge ($e$) in accordance with:

$$\Delta V = \frac{e}{C_{DL}} \quad (4)$$

where $C_{DL}$ is the double layer capacitance of single Au nanoparticle. The evolution of discrete charging states in Au$^{140}$ is due to the reduced $C_{DL}$ when core size is made smaller.
and reflects the emergence of non-continuous electronic energy state. This trend is even more obvious with smaller 1.1 nm Au$_{38}$ which exhibits step-like absorbance spectrum and an unevenly spaced voltammogram. A molecule-like band gap behavior is observed as seen from the large peak spacing between first oxidation and reduction peak in electrochemistry and agrees with the spectroscopically-measured band edge of ~1.3 eV. The electronic properties of Au$_{38}$ clearly justify itself as a well-defined redox moieties which can be manipulated in a fashion similar to the conventional molecular redox compounds in electron transfer studies.

1.3.2 Ligand Exchange Dynamics

As important as the core size, the organic monolayer of Au nanoparticles has substantial influence on their chemical, electronic and optical properties. A recent study by Rui et al. demonstrates that the inclusion of aromatic ligands in the monolayer of Au$_{38}$ nanoparticles has inductive effects on their electronic energy state. The organic monolayer of Au nanoparticles can be manipulated with choice of protective ligands in Brust synthesis or the directly functionalizing the end group of ligands. While those methods are only limited to a few number of ligands, a more general way to explore the chemistry of monolayer is by ligand exchange reaction.

The thiolate ligand exchange reaction on both Au$_{140}$ and Au$_{38}$ has been studied. It is observed that a) the reaction mainly follows the associative route with 1:1 stoichiometry of incoming and outgoing ligand; b) there exist two dynamic phases in exchange kinetics: the initial, rapid phase occurring on the vertex and possibly edge binding sites on core surfaces and the later, slower phase taking place on terrace sites; c) the exchange reaction is sensitive
Figure 1.7 UV-Vis spectra and cyclic voltammograms of monolayer-protected Au nanoparticles with different core size in dilute methylene chloride solution. A 1.6 mm Pt disk working electrode is used with supporting electrolyte of Bu$_4$NClO$_4$.\textsuperscript{35,36,38}
to the oxidation state of core: reactions are inhibited under Ar and accelerated when core oxidized; d) there is no obvious core size change.

While ligand exchange reaction has been carried out on different core size, all reaction involve only sulfur-based thiolate ligands. The ligand exchange reaction between thiolate ligands-protected Au\textsubscript{38} and phosphorous-based free triphenlphosphine ligands shows very different mechanism\textsuperscript{43}: the Au(I)-thiolate complex instead of free thiol is replaced out by the incoming ligands and the resulting Au nanoparticles have reduced core size. The observation of core size change is not a single event and indirectly supported by a separate experiment where triphenylphosphine stabilized Au\textsubscript{55}, when reacted with free thiols, gives an increased core size, Au\textsubscript{75}.\textsuperscript{44} The latter reaction can be regarded as the reverse reaction of the formal. The involvement of Au(I)-thiol complex in ligand exchange reaction is also not uncommon. Recently, a Au(I) thiolate complex, produced by oxidizing Au core, is identified as the carrier for ligand/core-metal in exchange reaction.\textsuperscript{42} Clearly, the ligand exchange reaction with phosphorous ligands, even though not able to well maintain the Au core size, provide insightful information on the ligand exchange dynamics which is crucial to the chemistry of monolayer-protected Au nanoparticles.
References:


2.1 Introduction

Our laboratory has designed a series of model semi-solid materials for the purposes of investigating the responses of electron transfer and mass transport dynamics to molecular environments that are amorphous and have slow time constants for mass and dipolar rearrangements. These materials consist of combinations of oligomeric (d.p. = 2 to 15 monomer units) polyether chains of appropriate length with molecular or ionic redox moieties. The combinations lead to highly viscous, amorphous, room temperature molecular melts or molten salts (or ionic liquids in contemporary parlance). The function of the polyether chains is to effect disorder of normally crystalline redox substances. These materials have modest ionic conductivities, but by exploiting microelectrode voltammetry, electrode reaction rates, rates of charge transport by electron-hopping reactions, and mass transport rates can be measured. The ruthenium complex studied here is:
where $X^-$ stands for perchlorate or its 8:2 or 7:3 mol:mol mixture with iodide. The substituent “R” provides the dis-organizing PEG ligand content, generating a viscous molten salt. The melt will be abbreviated as $[\text{Ru}(\text{bpy}(\text{CO}_2\text{MePEG}_{350})_2)_3][X]_2$.

In melts like the above, the Dahms-Ruff equation\(^3\) expresses the apparent diffusion coefficient ($D_{\text{APP}}$) for redox charge transport as a summation of the physical ($D_{\text{PHYS}}$) and electron ($D_E$) diffusion coefficients, the latter containing the electron self-exchange rate constant $k_{\text{EX}}$ of the Ru(III/II) redox couple of the $[\text{Ru}(\text{bpy}(\text{CO}_2\text{MePEG}_{350})_2)_3][X]_2$ melt:

$$D_{\text{APP}} = D_{\text{PHYS}} + D_E = D_{\text{PHYS}} + \frac{k_{\text{EX}}\delta^2 C}{6}$$  \hspace{0.5cm} (1)

where $\delta$ is the equilibrium center-to-center distance between electron donor and acceptor, and $C$ is total redox site concentration in the melts. From studies\(^4\) of the analogous Co complex, the PEG-tailed Ru metal complex has a small physical diffusivity in comparison to the rate of charge transport by electron hopping ($D_E$). As a consequence, when an electrode oxidation of Ru(II) complexes leads to a mixed valent layer of Ru(III/II) complexes around an electrode, serial electron self-exchange reactions between Ru(II) donors and Ru(III) acceptors serve to transport redox charge more rapidly than can physical diffusion of the
donor or acceptor.\textsuperscript{4,5} Additionally, and of crucial importance in the present study, the physical diffusivity of the Ru complex in the melt is small in comparison to that of its perchlorate counterion.\textsuperscript{5}

A motivation in our studies of hybrid redox polyether melts\textsuperscript{1,4,5} has been to understand the observation—dating from the days of electron transport investigations\textsuperscript{3a} in redox polymer films—that electron transfer rates ($k_{EX}$) in semi-solid media are generally smaller, and their thermal activation barriers larger, than those of similar donor-acceptor pairs in dilute, fluid solution.\textsuperscript{1a,f,4c,6} The electron transfer barrier energies in the semi-solid state redox materials are also larger than outer-sphere reorganization barrier energies predicted based on classical Marcus theory.\textsuperscript{7} Starting from observations in which electron transfer (ET) rate constants were correlated with the viscosity of the solvent,\textsuperscript{8} we explored the slower electron transfer rates and larger barrier energies with a hypothesis of ET rate control by solvent dynamics, i.e., slow and energetically costly repolarization of ether dipoles in the polyether “solvent shell” at rates reflected in segmental polyether chain motion control of physical mass transport.\textsuperscript{3,4b,6b,9}

Recent results in studies of cobalt and ruthenium complex-based molten salts where sorption by plasticizing carbon dioxide was exploited to manipulate melt transport properties have, however, produced an improved interpretation of ET rate control in these melts.\textsuperscript{10} Notably, the ET rate constants ($k_{EX}$) of redox ions were shown to correlate more closely with diffusion coefficients and activation barrier energies of their counterions than with corresponding diffusion coefficients and barrier energies of the redox moieties themselves. The improved interpretation has been labeled \textit{ion atmosphere relaxation} rate control. In this model, when donor-acceptor electron transfer occurs, there is a competition between back ET
and coulombically-driven redistribution of the charge compensating counterions. If the redistribution rate is fast, the net charge transport rates reflect the intrinsic ET reaction rates. If it is slower, the net charge transport rates instead reflect the rate of relaxation of the ion atmosphere around the reacting donor-acceptor pair. The latter circumstance appears to prevail in the hybrid polyether molten salts, and potentially in other semi-solid redox media.

Accurate measurement of diffusion rates of the melt counterions is crucial in assessing the ion atmosphere mechanism of ET control. In previous studies, the counterion diffusion coefficients were calculated from ionic conductivities of melts using the Nernst-Einstein relation:

\[ \sigma_{\text{ION}} = \frac{F^2}{RT} \left[ z_{\text{Ru}}^2 D_{\text{Ru}} C_{\text{Ru}} + z_{\text{ClO}_4}^2 D_{\text{ClO}_4} C_{\text{ClO}_4} \right] \]  

(2)

where \( z, D, \) and \( C \) are charge, diffusion coefficient, and concentration of the indicated species, respectively. The physical diffusion coefficient of the metal complex is measured using the Co(III/II) couple of a structurally analogous melt complex, and as noted above is usually negligibly small, i.e., the \( D_{\text{Ru}} \) term is dropped from Equation 1. The ionic conductivities are measured using AC impedance at potentials where the electrochemical reactions do not interfere.

While the above conductivity-based procedure is physically sound, it entails assumptions about ion pairing effects that would potentially under-estimate the value of \( D_{\text{ClO}_4} \). A direct measurement of counterion diffusivity would be an important control experiment. With that in mind, presented here is a scheme doing that, based on the electrochemical oxidation of iodide counterions of the Ru complex melts. The iodide diffusion coefficient is measured using chronoamperometry. The iodide is introduced into the \([\text{Ru(bpy(CO}_2\text{MePEG}_{350})_2]_3[X]_2\) melt by mixing pure melts having \( X = \text{ClO}_4^- \) and \( X = I^- \).
in proportions such that the mole fraction of iodide (20 and 30 mole %) is less than the percolation threshold for electron transport by ET of the iodide/tri-iodide redox couple (>40 mole%). The goal is a comparison of the diffusion coefficient derived from iodide chronoamperometry to the $D_{\text{CION}}$ derived from ionic conductivity of the melt mixture—which of course is an average diffusivity of the perchlorate and iodide counterions. The results of the comparison show very good agreement between the two, validating our approach of using ionic conductivity to measure $D_{\text{CION}}$ in previous studies.

A second purpose of the present study is an examination of charge transport in the \([\text{Ru(bpy(CO}_2\text{MePEG}_{350})_2]_3[X]_2\) melt, in relation to the ion atmosphere relaxation model. Measurements of the temperature dependent rate of ET in the Ru(III/II) couple of the \([\text{Ru(bpy(CO}_2\text{MePEG}_{350})_2]_3[X]_2\) melt are fully consistent with the ion atmosphere model of electron transport in semi-solid media. Values of $k_{\text{EX}}$ vary linearly with $D_{\text{CION}}$ in log-log plots, with unity slopes. Further, the Ru(III/II) results are superimposable on previous results for Co(II/I) ET, as expected if the intrinsic ET rate of the metal couple is not the source of charge transport rate control, but rather the ET rate is controlled by relaxation of the counterion atmosphere around the donor-acceptor couple.\textsuperscript{10}

2.2 Experimental

**Chemicals.** Ruthenium(III) chloride hydrate, silver perchlorate hydrate (99%), 1,4-benzoquinone (98%), diethylene glycol dimethyl ether (anhydrous, 99.5%), ethyl ether, iron(II) perchlorate hydrate (98%), Dowex 1x2-200 anion resin, sodium hydroxide solution (50%, w/w), hydriodic acid (55%, unstabilized), t-butyrammonium iodide (98%) were used
as received. The ligand bpy(CO$_2$MePEG$_{350}$)$_2$ was synthesized according to previous literature. $^{4a,5}$ [Ru(bpy)$_3$][PF$_6$]$_2$ was provided locally (Anthony M. Leone).

**Synthesis of [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ and [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][I]$_2$.** 5 mol equivalents of 4,4'-diMePEG$_{350}$ ester 2,2'-bipyridine (“tailed ligand”) were added to a Schlenk flask equipped with stir bar and dried at 60 °C under vacuum over night. 1 mol equivalent of ruthenium (III) chloride hydrate, 3 mol equivalent of silver perchlorate hydrate and 1 mol equivalent of 1,4-benzoquinone were combined with the tailed ligand. 25 mL diethylene glycol dimethyl ether as solvent was added and the mixture was refluxed under Ar for one hour. After cooling to room temperature, the solution was diluted with water, filtered through celite, and dialyzed (MWCO 500 cellulose membrane) for two days in darkness into pure water, to remove salts and excess tailed ligand. The product was rotary evaporated to yield a dark red oil, which was extracted (with stirring) in ethyl ether for 5-10 minutes to remove any remaining un-reacted ligand. The extraction was repeated till free ligand was undetectable by a test of the ether extract with filtrate paper soaked with an acetone solution of iron(II) perchlorate, which sensitively gave a pink color if ligand was present. In some preparations, an additional purification on a Brockman I neutral alumina column was used to remove a brown impurity; elution with acetonitrile separated the [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ as a red band from the (unknown) brown impurity. The purity was confirmed by $^1$H NMR and solution electrochemistry. [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][I]$_2$ was prepared from the perchlorate melt by ion exchange on Dowex 1x2-200 anion resin. 13 g dry resin mixed with 100 mL Nanopure water was placed in a column and converted to the OH$^-$ form (4 M NaOH) and then to the iodide form using 4 M HI, washing the column with pure water until the eluent was neutral pH. A
concentrated aq. solution of 0.75 g [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ was slowly passed through the column, rotary evaporating the eluent to yield a dark red oil.

Two different mixed-counterion Ru melts were prepared by mixing acetonitrile solutions of [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ and [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][I]$_2$ in mole ratios of 7:3 and 8:2. The solution concentrations prior to mixing were determined by UV-Vis spectroscopy based on known absorbance coefficients at 468 and 354 nm.$^{12}$ The acetonitrile was removed by rotary evaporation.

**Preparation of [Ru(bpy)$_3$][I]$_2$.** A concentrated acetone solution of 10 mol equivalents of tetra-butylammonium iodide was mixed with 1 mol equivalent of [Ru(bpy)$_3$][PF$_6$]$_2$, which precipitated the iodide salt over a period of stirring for 10 minutes. The solid was filtered, washed with acetone and thoroughly dried in vacuum.

**Solution Electrochemistry.** Cyclic voltammetry (CV) was performed in degassed acetonitrile/Bu$_4$NClO$_4$ with 0.4 mm diameter platinum (Pt) working, 0.5 mm diameter Ag quasi-reference (QRE) and Pt auxiliary electrodes. The electrodes were the wire tips of the assembly described below. Voltammetry was recorded with a Bioanalytical System (BAS) Model 100B potentiostat.

**Electrochemical Measurements in Undiluted Ruthenium Complex Melts.** Cyclic voltammetry, chronomperometry and ionic conductivity measurements of the undiluted ruthenium complex melts were performed on films of the melts on the platform of a previously described four-electrode assembly,$^{10}$ which contains a 25 µm diameter Pt microelectrode, a silver quasi-reference electrode and two 0.4 mm diameter Pt electrodes. The cyclic voltammetry and chronomperometry in the melts were done with the microelectrode as working electrode. Ionic conductivity was based on the A.C. impedance of
the film between the two 0.4 mm diameter Pt wires. The platform assembly was polished with successively smaller grades (down to 0.05 µm) of alumina and sonicated in water and ethanol, respectively. The electrodes are further electrochemically cleaned in 0.1 M H$_2$SO$_4$ solution and then washed with water and dried in air prior to use.

A thin film of thoroughly dried Ru complex melt was cast onto the platform of the electrode assembly and further dried under vacuum (ca. 1x10$^{-3}$ Torr) at 70 °C for at least 24 hours prior to measurement. Two hours were required for thermal equilibrium between the film and cell in temperature dependency experiments, controlling the temperature with a Neslab Model RTE-140 circulating bath.

Cyclic voltammetry (CV) and potential step chronoamperometry were performed using a home-built low-current potentiostat and locally written data acquisition software. The small ionic conductivities of the Ru metal complex necessitate the use of the microelectrode and slow potential scan rates in CV to avoid distortion from $iR_{\text{UNC}}$. CV was used to determine the locations of the current peaks, and potential steps of 400-500 mV from a non-Faradaic region to a diffusion-limited potential of the wave were applied for 120—300 s. The recorded current-time data were iteratively fitted into the Shoup-Szabo equation:

$$I = 4nF r D_{\text{app}} C \left[ 0.7854 + \frac{0.8862}{t^{1/2}} + 0.2146e^{-0.7823/t^{1/2}} \right]$$

(3)

where $I$ is the current, $F$ Faraday’s constant, $r$ the microelectrode radius, and $t$ is time. An example is shown in Figure 2.1. The diffusion geometry is close to linear.

**Ionic Conductivity Measurement.** Ionic conductivity was measured using a Solartron Model SI 1260 impedance/gain phase analyzer—SI 1287 electrochemical interface combination over a frequency range from 500 kHz to 1 Hz for Ru complex melts. The dc
bias was held at the rest potential while the ac amplitude was set to 20-50 mV. Conductivity was calculated as the ratio of geometric cell constant (calibrated by standard solutions) and cell resistance (taken from the low-frequency real-axis intercept of the complex impedance semicircle).

2.3 Results and Discussion

2.3.1 Voltammetry of the Ru Complex in Dilute Acetonitrile Solution.

Figure 2.2A shows the familiar\(^{15}\) reversible cyclic voltammetry of a dilute solution of [Ru(bpy)\(_3\)][PF\(_6\)]\(_2\). The Ru(III/II) wave lies 2.6 V positive of the first of the three negative potential reductions that correspond to successive reductions of the bipyridine ring ligands. When the Ru complex counterion is iodide (Figure 2.2B), the Ru complex voltammetry is the same, except for the super-position of a wave due to iodide oxidation that is well resolved from the Ru(III/II) voltammetry. The iodide reaction is thought to be a two-step process:\(^{16}\)

\[
\begin{align*}
3I^- - 2e^- & \rightarrow I_3^- \\
2I_3^- - 2e^- & \rightarrow 3I_2
\end{align*}
\]  

(4)

Iodide voltammetry identical to that in Figure 2.2B was observed in acetonitrile solutions of tetrabutylammonium triiodide. In the voltammetry, the first oxidation wave is much less reversible than the second one, an effect thought\(^{17}\) to be related to iodide adsorption on the Pt electrode surface. The dilute solution voltammetry in Figure 2.2 is substantially duplicated in CV’s of the tailed Ru complexes in which perchlorate or iodide were counterion (Figure 2.3). The shift in the potentials of the Ru redox couples expected from the ester substituents on the tailed bipyridine rings\(^5\) is masked by our choice of the \(E^0[\text{Ru(III/II)}]\) as reference in the potential axis.
Figure 2.1 Chronoamperometric current-time response curve for stepping over the first oxidation wave of iodide, in an undiluted $[\text{Ru} \text{(bpy)} \text{(CO}_2 \text{MePEG}_{350})_2]^2\text{X}_2$ melt in which 30% of the counterions are iodide and 70% are perchlorate. 13 µm radius Pt microdisk electrode, at 50°C. The solid line (---) is given by iterative fitting of experimental data (•••) to equation (3).
2.3.2 Voltammetry of Undiluted Ru Complex Melts

Voltammetry of the Ru(III/II) wave of the undiluted [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ melt is shown at a series of temperatures in Figure 2.4. The voltammetry is consistent with a previous study$^5$ in which the value of $D_{\text{PHYS}}$ in this melt was demonstrated to be insignificant in relation to $D_{\text{APP}}$. That is, the currents in Figure 2.4 are dominated by charge transport via Ru(III/II) electron self-exchange reactions in the concentrated, electrochemically generated mixed valent film at the electrode/melt interphase. Observation of the Ru(III/II) wave in the undiluted iodide salt melt ([Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][I]$_2$) was expectedly unsuccessful. The iodide oxidation, equation (4), precedes the Ru(III/II) reaction (Figure 2.3), producing a neutral product, so that the interphase region is starved of mobile, charge-compensating counterions and thus becomes extremely resistive.

The voltammetry of the two mixed melts of [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ and [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][I]$_2$ was in contrast, well behaved as shown in Figure 2.5 and 2.6 at a series of temperatures. The voltammetric pattern is similar to that in Figure 2.3, except that the iodide oxidation is much less reversible. (The cathodic currents rising at the far right are the beginning of the reverse waves in the iodide voltammetry.) The two steps of iodide oxidation remain reasonably well-resolved above about 45 °C.

2.3.3 Counterion Transport Measurements.

The diffusion coefficients $D_{\text{CION}}$ of the counterions in the [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ and mixed counterion [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][X]$_2$ melts were calculated from ionic conductivities measured by AC impedance, as noted above.
The conductivities and $D_{CION}$ results for a range of temperatures of the three melts are shown in Tables 2.1-2.3. The $D_{CION}$ results for the mixed melts of course represent an average value for the ClO$_4^-$ and I$^-$ counterions in their mixtures. The AC impedance spectra displayed no features that would suggest a mixture of strongly differing conductivity impedances.

Diffusion coefficients for iodide were also measured using potential step chronoamperometry, stepping from the double layer region (see arrows Figure 2.5) to potentials either at which iodide is oxidized to triiodide (I$_3^-$) or to those producing iodine (I$_2$) (Equation 4). Data from the former, $D_{I,I3}$, should be more reliable than $D_{I,I2}$, since the background current corrections are smaller. An example of analysis of a current-time response is shown in Figure 2.1, and $D_{CION}$ results are given in Tables 2.1 to 2.3. Tables 2.2 and 2.3 show that the $D_{I,I3}$ and $D_{I,I2}$ results are in reasonable agreement with one another, well within a factor of two.

Tables 2.2 and 2.3 also show that the $D_{I,I3}$ and $D_{I,I2}$ results agree quite well with the $D_{CION}$ results. Tables 2.2 and 2.3 (last line) give ratios $D_{CION}/D_{I,I3}$ of the conductivity-measured $D_{CION}$ and the iodide oxidation-measured $D_{I,I3}$; the agreement is within 20% except for the two lowest temperatures in Table 2.2. For diffusion coefficients measured with such different procedures, this agreement is in fact, excellent. The $D_{CION}$ measurement is a weighted average of diffusion rates of ClO$_4^-$ and I$^-$ counterions, with ClO$_4^-$ being the more populous ion. The agreement of $D_{CION}$ with $D_{I,I3}$ thus further argues that the two counterion diffusion coefficients must be quite similar. The agreement between the differently determined diffusion coefficients provides an important validation of our past procedure of using conductivity-derived counterion diffusion coefficients.

The activation barriers for counterion transport in the two mixed melts as obtained
Figure 2.2 25°C cyclic voltammetry (300 mV/s) of (A) 1.5 mM [Ru(bpy)$_3$][PF$_6$]$_2$ and (B) 1.0 mM [Ru(bpy)$_3$][I]$_2$ in acetonitrile/Bu$_4$NClO$_4$ solution at a 0.4 mm diameter Pt disk working electrode. The potentials are referred to the formal oxidation potential (1.29 V vs. SCE) of ruthenium tris-bipyridine in acetonitrile to avoid the influence of iodide on the silver quasi-reference electrode.$^{28}$
**Figure 2.3** 25°C cyclic voltammetry (100 mV/s) of (A) 1.2 mM [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ and (B) 2.0 mM [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][I]$_2$ in acetonitrile/Bu$_4$NClO$_4$ solution at 0.4 mm diameter Pt disk working electrode. The potentials are referred to the formal oxidation potential (1.63 V vs. SCE) of [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ in acetonitrile.$^5$
**Figure 2.4** Cyclic voltammetry of the Ru(II/III) couple (25 mV/s) in an undiluted [Ru(bpy(CO₂MePEG₃₅₀)₂)₃][ClO₄]₂ melt, 13 µm radius Pt microdisk working electrode and indicated temperatures. The insert shows the complete cyclic voltammogram of [Ru(bpy(CO₂MePEG₃₅₀)₂)₃][ClO₄]₂ melt at 70°C; the reduction wave for Ru(II/I) electron transfer reaction is distorted by resistance effects. The formal oxidation potential (1.63 V vs. SCE) of [Ru(bpy(CO₂MePEG₃₅₀)₂)₃][ClO₄]₂ in acetonitrile is taken as potential reference.
Potential $V$ vs. $E^{\circ}[\text{Ru(III/II)}]$
Table 2.1 Transport and ionic conductivity measurement of undiluted [Ru(bpy(CO₂MePEG₃50)₂)]₂[ClO₄]₂ melts at different temperatures.
<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>45</th>
<th>50</th>
<th>55</th>
<th>60</th>
<th>65</th>
<th>$E_A$, kJ/mol</th>
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<tr>
<td>$D_{APP}^a$, $10^{-9}$ cm$^2$/s</td>
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<td>7.3</td>
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<td>$k_{EX}^b$, $10^6$ M$^{-1}$s$^{-1}$</td>
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<td>4.1</td>
<td>5.4</td>
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</tr>
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<td>$\sigma^c$, $10^{-6}$ mhos$^{-1}$cm$^{-1}$</td>
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<td>8.7</td>
<td>11</td>
<td>14</td>
<td>17</td>
<td>42</td>
</tr>
<tr>
<td>$D_{ClO_4}^d$, $10^{-9}$cm$^2$/s</td>
<td>2.2</td>
<td>2.9</td>
<td>3.7</td>
<td>4.8</td>
<td>6.0</td>
<td>45</td>
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<tr>
<td>$D_{ClO_4}/D_E$</td>
<td>0.71</td>
<td>0.69</td>
<td>0.67</td>
<td>0.66</td>
<td>0.62</td>
<td>—</td>
</tr>
</tbody>
</table>

$^a$ Diffusion coefficient measurements based on chronoamperometry of the Ru(III/II) reaction and Shoup-Szabo fitting to the experimental current-time curves. $^b$ Calculated from equation 1 assuming negligible $D_{PHYS}$. The density of ruthenium melts is measured as 1.32 g/cm$^3$, giving the concentration of ruthenium complex as 0.435 M (MW=3024 g/mol). The average redox center-to-center distance, $\delta$ (1.56 nm at room temperature), was estimated on the basis of a cubic lattice relation $\delta^3 = 1/(N_A C)$, where $N_A$ is Avogadro’s constant. $^c$ From AC impedance measurement. $^d$ Calculated from equation 2 assuming $D_{Ru}$ is negligible.
Table 2.2  Transport and ionic conductivity measurement of undiluted [Ru(bpy(CO₂MePEG₃₅₀)₂)[X]₂ melts in which the mole ratio of iodide and perchlorate counter ions is 2:8 (i.e., 20% of X is iodide).
<table>
<thead>
<tr>
<th></th>
<th>45</th>
<th>50</th>
<th>55</th>
<th>60</th>
<th>65</th>
<th>( E_A ), kJ/mol</th>
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<tbody>
<tr>
<td>( D_{\text{APP}} ), ( 10^{-9} \text{cm}^2/\text{s} )</td>
<td>6.6</td>
<td>8.1</td>
<td>10</td>
<td>13</td>
<td>16</td>
<td>41 (41)</td>
</tr>
<tr>
<td>( k_{\text{EX}} ), ( 10^6 \text{M}^{-1}\text{s}^{-1} )</td>
<td>3.7</td>
<td>4.6</td>
<td>5.7</td>
<td>7.2</td>
<td>9.2</td>
<td>41 (5.8)</td>
</tr>
<tr>
<td>( D_{\text{I,I}_3} ), ( 10^{-9} \text{cm}^2/\text{s} )</td>
<td>1.0</td>
<td>1.8</td>
<td>2.7</td>
<td>3.8</td>
<td>5.2</td>
<td>63 (8.8)</td>
</tr>
<tr>
<td>( D_{\text{I,I}_2} ), ( 10^{-9} \text{cm}^2/\text{s} )</td>
<td>1.5</td>
<td>2.5</td>
<td>4.0</td>
<td>5.7</td>
<td>7.5</td>
<td>67 (11)</td>
</tr>
<tr>
<td>( \sigma ), ( 10^{-6} \text{mhos}^{-1}\text{cm}^{-1} )</td>
<td>5.6</td>
<td>7.2</td>
<td>9.2</td>
<td>12</td>
<td>14</td>
<td>42 (14)</td>
</tr>
<tr>
<td>( D_{\text{ClO}_4} ), ( 10^{-9} \text{cm}^2/\text{s} )</td>
<td>1.8</td>
<td>2.4</td>
<td>3.1</td>
<td>4.0</td>
<td>5.0</td>
<td>45 (13)</td>
</tr>
<tr>
<td>( t_{\text{ClO}_4} )</td>
<td>0.88</td>
<td>0.84</td>
<td>0.82</td>
<td>0.81</td>
<td>0.79</td>
<td>42 (6.6)</td>
</tr>
<tr>
<td>( D_{\text{ClO}_4}/D_E )</td>
<td>0.27</td>
<td>0.30</td>
<td>0.31</td>
<td>0.31</td>
<td>0.31</td>
<td>42 (7.1)</td>
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<tr>
<td>( D_{\text{ClO}<em>4}/D</em>{\text{I,I}_3} )</td>
<td>1.8</td>
<td>1.3</td>
<td>1.1</td>
<td>1.0</td>
<td>1.0</td>
<td>42 (7.1)</td>
</tr>
</tbody>
</table>

\( a \) \( D_{\text{APP}} \) values in parenthesis are corrected for electronic migration. \( b \) Obtained in chronoamperometry with a potential step to the oxidation of iodide to triiodide. \( c \) Obtained in chronoamperometry with a potential step to the oxidation of iodide to iodine. \( d \) Calculated from equation 2 assuming \( D_{\text{Ru}} \) is negligible and averaging the diffusion coefficients of perchlorate and iodide as \( D_{\text{ClO}_4} \). \( e \) The transference number for perchlorate.
Table 2.3  Transport and ionic conductivity measurement of undiluted [Ru(bpy(CO2MePEG$_{350}$)$_2$)$_3$][X]$_2$ melts in which the mole ratio of iodide and perchlorate counter ions is 3:7 (i.e., 30% of X is iodide).
<table>
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<th>$T$, °C</th>
<th>45</th>
<th>50</th>
<th>55</th>
<th>60</th>
<th>65</th>
<th>$E_A$, kJ mol$^{-1}$</th>
</tr>
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<tr>
<td>$D_{APP}^a$, $10^{-9}$ cm$^2$/s</td>
<td>5.7</td>
<td>7.0</td>
<td>8.8</td>
<td>11</td>
<td>15</td>
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<td>($4.9$)</td>
<td>($6.0$)</td>
<td>($7.6$)</td>
<td>($9.5$)</td>
<td>($13$)</td>
<td></td>
<td>($42$)</td>
</tr>
<tr>
<td>$k_{EX}$, $10^6$ M$^{-1}$s$^{-1}$</td>
<td>3.2</td>
<td>3.9</td>
<td>5.0</td>
<td>6.3</td>
<td>8.3</td>
<td>42</td>
</tr>
<tr>
<td>$D_{I,I3}^b$, $10^{-9}$ cm$^2$/s</td>
<td>1.3</td>
<td>1.9</td>
<td>2.9</td>
<td>3.9</td>
<td>5.2</td>
<td>63</td>
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<tr>
<td>$D_{I,I2}^c$, $10^{-9}$ cm$^2$/s</td>
<td>1.6</td>
<td>2.3</td>
<td>3.3</td>
<td>5.0</td>
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<td>69</td>
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<tr>
<td>$\sigma$, $10^{-6}$ mhos$^{-1}$cm$^{-1}$</td>
<td>4.7</td>
<td>6.1</td>
<td>7.7</td>
<td>9.7</td>
<td>12</td>
<td>42</td>
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<tr>
<td>$D_{ClO4}^d$, $10^{-9}$ cm$^2$/s</td>
<td>1.5</td>
<td>2.0</td>
<td>2.6</td>
<td>3.3</td>
<td>4.2</td>
<td>45</td>
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<tr>
<td>$t_{ClO4}^e$</td>
<td>0.73</td>
<td>0.71</td>
<td>0.68</td>
<td>0.66</td>
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<tr>
<td>$D_{ClO4}/D_E$</td>
<td>0.26</td>
<td>0.29</td>
<td>0.30</td>
<td>0.30</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>$D_{ClO4}/D_{I,I3}$</td>
<td>1.2</td>
<td>1.0</td>
<td>0.9</td>
<td>0.9</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $D_{APP}$ values in parenthesis are corrected for electronic migration. $^b$ Obtained in chronoamperometry with a potential step to the oxidation of iodide to triiodide. $^c$ Obtained in chronoamperometry with a potential step to the oxidation of iodide to iodine. $^d$ Calculated from equation 2 assuming $D_{Ru}$ is negligible and averaging the diffusion coefficients of perchlorate and iodide as $D_{ClO4}$. $^e$ The transference number for perchlorate.
from Arrhenius plots (Figure 2.7) are listed in Tables 2.2 and 2.3. Table 2.1 shows activation barrier energies for $D_{\text{CION}}$ in the pure $X = \text{ClO}_4^-$ melt; these data agree with the $D_{\text{CION}}$ values in Tables 2.2 and 2.3. The $E_A$ results for $D_{\text{CION}}$ and $D_{\text{I,I3}}$ are somewhat different, thermal barrier energies for the latter being larger, but the results are somewhat approximate owing to the small temperature range studied, and considering the slight downward curvature in the $D_{\text{I,I3}}$ activation plots at the lowest temperatures. Such curvature has been seen previous experiments conducted over wider temperature ranges,\(^{4a}\) and is classically understood by strong coupling between physical transport and polyether chain segmental motions. The coupling may be stronger for iodide than ClO$_4^-$ given the lack of noticeable curvature in Figure 2.7 for the latter ion. The differences in the actual diffusion coefficients in Figure 2.7 are nonetheless minor (Tables 2.2 and 2.3).

### 2.3.4 Electron Hopping Transport Measurements.

$D_{\text{APP}}$ for the Ru(III/II) reaction was measured using potential step chronoamperometry. The initial potential for the step (see Figure 2.5) is near the foot of the Ru(III/II) oxidation wave, which for the mixed counterion [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][X]$_2$ melts lies between the iodide and Ru(III/II) oxidation waves. The initial potential was applied for 600 seconds before the step in order to allow currents from the iodide oxidation reactions to achieve a small, steady value.\(^{19}\) Results for $D_{\text{APP}}$ in the [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][ClO$_4$]$_2$ melt are given in Table 2.1 and those for the mixed counterion [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][X]$_2$ melts in Tables 2.2 and 2.3. The results in Tables 2.1-2.3 show that $D_{\text{APP}}$ is substantially the same in the three melts, well within a factor of two. That is, the electron transport properties of the Ru(III/II) melts are
**Figure 2.5** Cyclic voltammetry (25 mV/s) of an undiluted \([\text{Ru(bpy(CO}_2\text{MePEG}_{350})_2]}\text{[X]}_2\) melt, where \(X = \text{ClO}_4^-\) and \(I^-\) in a 7:3 mole ratio. Voltammetry obtained at a 13 µm radius Pt microdisk working electrode, at indicated temperatures. The potential reference is the same as Fig.4.
Potential /V vs. E°[Ru(III/II)]

2 nA

- I⁻ to I₃⁻
- I⁻ to I₂
- Ru(II) to Ru(III)

Temperature:
- 65°C
- 60°C
- 55°C
- 50°C
- 45°C
Figure 2.6 Cyclic voltammetry (50 mV/s) of an undiluted [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][X]$_2$ melt, where $X = \text{ClO}_4^-$ and $\Gamma$ in a 8:2 mole ratio, at 13 µm radius Pt microdisk electrode at indicated temperatures. The positive potential scan is reversed prior to the Ru(II/III) wave. The potential reference is the same as Fig.4.
Potential /V vs. $E^{0'}[\text{Ru(III/II)}]$
substantially unaffected by whether the counterion is solely $X = \text{ClO}_4^-$ versus a mixed $\text{ClO}_4^-/\Gamma$ counterion melt. This result must be viewed against the background that (vide supra) the diffusion coefficients of the two counterions are nearly identical. There are some differences between the activation barrier energies for the pure versus mixed counterion melts; again we point to the small temperature range employed with consequent uncertainty in the barrier data. Tables 2.1-2.3 also give the apparent electron self-exchange rate constants $k_{\text{EX}}$ obtained from $D_{\text{APP}}$ using equation 2.

If the electron hopping mobility in a melt exceeds that of the charge compensating counterion, potential gradients develop that can accelerate the electron hopping rate. This is the case as seen from the $< 1$ ratios of $D_{\text{CION}}/D_E$ given in Tables 2.2 and 2.3. The effect is called electronic migration, and can be corrected for as described previously. The corrected $D_{\text{APP}}$ values, given in parenthesis in Tables 2.2 and 2.3, show that the correction is a small effect. That is, electronic migration effect is not a significant consideration.

2.3.5 Comparison to the Ion Atmosphere Relaxation Model.

As noted above, an electron transfer reaction redistributes charge. The ET must be accompanied by the usual repolarization of solvent dipoles, according to classical ET theory. In addition, the redistribution of charge favors the reverse ET reaction unless the coulombic imbalance is relieved by a redistribution of the charge compensating counterions. In a fluid medium, the large mobility of the counterions, and the fact that they are often in great excess, ensures that the ionic atmosphere relaxation occurs rapidly. In a semi-solid medium like the redox polyether hybrid melts, however, there is neither a large excess of indifferent neighbor ions nor a high physical mobility of them. For the Ru complex melt, the
Figure 2.7 Arrhenius plots of $D_{\text{ClO}_4}$ (●) and $D_{\text{I,I}_3}$ (■) from undiluted [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][X]$_2$ melts in which the percentage of iodide in the iodide/perchlorate mixture is (A) 20% and (B) 30%.
situation can be schematically represented as:

\[
X^\cdot \text{Ru}^{III}\text{Ru}^{II} \xrightarrow{k_1} X^\cdot \text{Ru}^{II}\text{Ru}^{III} \xrightarrow{k_2} \text{Ru}^{II}\text{Ru}^{III}X^-
\]

where the right hand reaction is the ion relaxation process. Using a steady-state approximation, and drawing analogy of the (intrinsically ion paired) melts with a treatment of ion-pairing effects on ET, one has the relation:

\[
k_{EX} = \frac{k_1 k_2}{k_2 + k_{-1}}
\]

in which \(k_1\) and \(k_2\) are the forward and back ET rate constants and the counter ion relaxation rate constant \(k_2\) is given by

\[
k_2 = D_{CION} \left( \frac{\pi}{2a} \right)^2
\]

where \(a\) is the counter ion diffusion length. When \(k_{-1} > k_2\), i.e., the overall ET rate control becomes not the intrinsic ET step itself, but instead the relocation of counter ions:

\[
k_{EX} = \frac{k_1}{k_{-1}} k_2 = K_{eq} k_2 = K_{eq} D_{CION} \left( \frac{\pi}{2a} \right)^2
\]

The electron transfer rate constant is then proportional to the diffusion coefficient of the counter ions.

A signature of this form of ET rate control is a linear relation between \(k_{EX}\) for the melt reaction (Ru(II/III)) and \(D_{CION}\). The results from the present study—the pure \(X = \text{ClO}_4^-\) and the two mixed counterion melts—are shown in Figure 2.8A. The plots are linear and within 10% of unity slope in all three cases, consistent with the above ion atmosphere relaxation model. The model additionally predicts that for similar ET reactions, i.e., same donor-acceptor reactant dimensions and similar \(K_{EQ}\) values, the experimental values of \(k_{EX}\) should
be independent of the metal of the complex (since $k_{\text{EX}}$ reflects counterion diffusion not intrinsic ET dynamics). Figure 2.8B shows the Ru melt data co-plotted with a previously reported\cite{10a,b,24} collection of data for the Co(II/I) ET reaction in Co complex melts having a similar structure. Clearly there is good orders-of-magnitude agreement, supporting ion atmosphere control.

The roughly two-fold difference between $D_{\text{I},3}$ and $D_{\text{Cl}^{-}}$ can be expressed in terms of a difference in the equilibrium constant of Equation 5 for $X = \text{iodide}$ versus perchlorate ion. Estimating the equilibrium constant from the intercept of Figure 2.8A was done by estimating the diffusion length value, $a$, for the counterion in a successful electron transfer process\cite{25}

$$a = \sqrt{2D\tau} \quad (9)$$

where $D$ is the diffusion coefficient of counter ions and $\tau$ the time scale for electron hopping.

$$\tau = \frac{1}{k_{\text{EX}}[Ru^{II}]} \quad (10)$$

A simple calculation based on the data in Table 2.1 gave $a \approx 0.75 \text{ nm}$ and 0.48 for perchlorate and iodide, respectively, both shorter than the 1.6 nm center-to-center distance in ruthenium perchlorate melts.\cite{26} The equilibrium constants obtained are 1.6 and 2.0, respectively.
Figure 2.8 (A) Relationship between apparent $k_{EX}$ for Ru(II/III) reaction and $D_{CION}$ measured at various temperatures in [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][X]$_2$ melts. Slopes are 1.1 (●), 0.90 (■) and 0.93 (▲) respectively. (B) The data in (A) ● co-plotted with literature data from liquid CO$_2$ plasticized melts, [Co(phen)$_3$](MePEG$_{350}$SO$_3$)$_2$\textsuperscript{10b} (▽) and [Co(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$](ClO$_4$)$_2$\textsuperscript{10a} (▼), MePEG350 plasticized melt [Co(phen)$_3$](MePEG$_{350}$SO$_3$)$_2$\textsuperscript{24} in mole ratio of 6:1 (○), 3:1 (□) and 2:1 (△), and [Co(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$](ClO$_4$)$_2$+xLiClO$_4$\textsuperscript{4b} (■) (x=0~1.31). The overall slope for the $D_{CION}$ correlation is 1.0.
Data Set From Plot A
References


12. Masui, H.; Murray, R. W. *Inorg. Chem.* 1997, 36, 5118. The dilute solution UV-Vis spectrum of \([\text{Ru}^{\text{II}}(\text{bpy})_2(\text{CO}_2\text{MePEG}_{350})_2]^{2+}\) exhibits two sets of charge transfer bands, 468 and 354 nm, which, assigned to \(\text{Ru} \rightarrow \text{tailed-bpy} \pi^*\) (1) and \(\text{Ru} \rightarrow \text{tailed-bpy} \pi^*\) (2), have the distinguish coefficients of 25,800 and 18,900 M\(^{-1}\)cm\(^{-1}\), respectively.


14. The radius of microelectrode, \(r\), was calibrated as 13µm in cyclic voltammogram of standard acetonitrile solution of ferrocene with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte according to \(i_{\text{Lim}} = 4nFrDC\).


19. This reaction leads to neutralization of iodide counter ions in melts around the electrode. Therefore, the melt in which the iodide is the only counter ion, \([\text{Ru}(\text{bpy})(\text{CO}_2\text{MePEG}_{350})_2]^2\)\(^{-}\), becomes very resistive and good voltammetry of the Ru(II/III) reaction could not be obtained.


26. The average redox center-to-center distance, δ, is 1.56 nm at room temperature (Ref. 5).
CHAPTER III
REACTION OF TRIPHENYLPHOSPHINE WITH
PHENYLETHANETHIOLATE-PROTECTED AU$_{38}$ NANOPARTICLES

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3.1 Introduction

Interest in monolayer-protected metal clusters (MPCs)$^1$ is fueled by a general attention to nanoscopic materials and by the promise of MPCs in applications in catalysis,$^2$ nanoscale electronic devices,$^3$ and chemical sensors.$^4$ Size-dependent MPC$^5$ electronic and optical properties offer further impetus for fundamental science. The synthetic route introduced by Brust et al.$^6$ was important in giving access$^1,7$ to alkanethiolate-protected Au clusters with core diameters < 5 nm, as well as by a general MPC stability that is conducive to further synthetic elaboration$^1$ of the thiolate monolayer shell while preserving the core size. Use of terminally functionalized alkanethiolate ligands allows$^8$ subsequent further elaboration of the monolayer, such as by amide or ester coupling to diverse other chemical moieties.$^9$ Modification of the MPC monolayer can be pursued by ligand place-exchange reactions,$^{4f,10}$ much as one might modify the ligands of a large, modestly labile metal complex. Such ligand exchanges have been widely explored.$^{4f,10}$ Thiolate-for-thiolate ligand
exchange is an associative process with 1:1 stoichiometry according to kinetic investigations of reactions of MPCs with thiols. Under mild conditions, the displaced ligand appears as a free thiol (as opposed to production of disulfide or oxidized sulfur products). The centrality of ligand exchange in the chemistry of Au nanoparticles makes understanding its chemistry a significant topic.

Phosphine-capped Au nanoparticles were described in 1981 by Schmid et al. and triphenylphosphine (PPh₃) and related phosphines have since experienced considerable study in Au nanoparticle chemistry. An important application has been in labeling reagents for biological electron microscopy. Phosphine is a reasonably strong electron donor for Au nanoparticles, increasing the core electron density and upwardly shifting the Fermi level. Phosphine ligands are at the same time rather labile; intermediate sized Au clusters (Au₃₂₋₃₆, Au₅₅(PPh₃)₁₂Cl₆ and Au₁₀₁(PPh₃)₂₁Cl₅) undergo rapid exchange (t₁/₂ ~sec to min). The smaller Au₁₁(PPh₃)₆Cl₃ seems less reactive.

Understanding phosphine-stabilized Au nanoparticles has been complicated by the tendency for rapid phosphine ligand dissociations and associated instability in dilute solutions and at elevated temperature. Hutchison et al. exploited phosphine ligand lability to convert the molecule-like Au₁₁(PPh₃)₇Cl₃ and Au₅₅(PPh₃)₁₂Cl₆ nanoparticles to thiolated-protected MPCs by exchange reactions with excess thiol. The resulting MPCs proved to be more stable than their phosphine-capped precursors. The phosphines of Au₅₅ nanoparticles can also be replaced by amines, but with an accompanying substantial increase in nanoparticle diameter. Chen et al. synthesized n-dodecanethiol-protected undecagold clusters through ligand exchange with Au₁₁(PPh₃)₇Cl₃ at varied feed ratios. The

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electronic properties of the products were sensitive to the nature of the surface-protecting ligands.\textsuperscript{14b}

This chapter examines the \textit{reverse} of the reactions reported by Hutchison\textsuperscript{18b, 20} and Chen,\textsuperscript{14b} i.e., reactions in which thiolates on \( \text{Au}_{38} \) MPCs are replaced by phosphines. Our aim is not to synthesize phosphine-capped nanoparticles but to shed further light on nanoparticle ligand exchange chemistry. The reverse reaction’s behavior produced significant observations. Observing the reaction of \( \text{PPh}_3 \) (as an in-coming ligand) with the molecule-like\textsuperscript{7b,21} 1.1 nm (dia.) \( \text{Au}_{38}(\text{SC}_2\text{Ph})_{24} \) MPC with UV-Vis and NMR spectrometries showed that the reaction is \textit{not simply an exchange of ligands} bonded to an unchanging \( \text{Au} \) nanoparticle core. Instead, the reaction, in its earliest stage, results in loss of one \( \text{Au} \) atom, as a \( \text{Au}^1\text{SC}_2\text{Ph} \) complex, from the \( \text{Au} \) MPC core for each reacting \( \text{PPh}_3 \) ligand. The loss of \( \text{Au}^1\text{SC}_2\text{Ph} \) leaving groups leads, in short order, to instability of the nanoparticle, as when the \( \text{PPh}_3 \) ligand is presented in large (\( \geq 10 \)-fold) excess to the \( \text{Au}_{38} \) MPC core.

### 3.2 Experimental

**Chemicals.** Hydrogen chloroaurate\textsuperscript{22} was prepared as described before. Triphenylphosphine (Aldrich, 99\%), methylene chloride (Fisher, 99.9\%), deuterated-methylene chloride (Cambridge Isotope Laboratories, Inc., 99.9\%), 1,4-benzoquinone (Aldrich, 98\%) and other chemicals were used as received.

**Synthesis of \( \text{Au}_{38}(\text{SC}_2\text{Ph})_{24} \).** Phenylethanethiolate-protected \( \text{Au}_{38} \) clusters were prepared as before\textsuperscript{7b} using the Brust procedure.\textsuperscript{6} Briefly, \( \text{HAuCl}_4 \) was phase-transferred from water to toluene by tetra-\( n \)-octylammonium bromide, then three equivalents of phenylethanethiol were added leading to a clear \( \text{Au}^1\text{thiolate} \) complex solution. Ten equivalents of \( \text{NaBH}_4 \) in 60 mL
water were added rapidly to the toluene solution which instantly became dark. The solution was stirred vigorously for 24 hours at 0°C; the toluene portion was separated, dried in vacuum, and re-dissolved in methanol. The cluster was precipitated from the methanol solution and collected on a glass frit. The \( \text{Au}_{38}(\text{SC}2\text{Ph})_{24} \) MPC was extracted from the reaction product with acetonitrile.

**Preparation of Au\(^{I}\)SC2Ph Complex.**\(^{23} \) 30 µl phenylethanethiol (HSC2Ph) was gradually added with stirring to 30 mg HAuCl\(_4\) in 5 ml THF. The yellow solution cleared and a white material precipitated, which was filtered on a glass frit and carefully washed with at least 30 ml THF. The white material was not allowed to dry out, since dried Au\(^{I}\)SC2Ph resists re-dissolution. A saturated CH\(_2\)Cl\(_2\) solution of the Au\(^{I}\)SC2Ph complex was made by dissolving the white material from the frit.

**Measurements.** Cyclic (CV) and differential pulse voltammetries (DPV) were conducted in a 25ml electrochemical cell with a 1.6 mm-diameter Pt disk working, Ag wire quasi-reference (QRE) and Pt auxiliary electrodes, controlled by an electrochemical workstation (CH Instruments, CHI660A), in a darkened Faraday cage, and under Ar when negative potentials were accessed. 1,4-Benzoquinone (BQ/BQ\(^{-}\))\(^{24} \) was used as an internal reference for the Ag QRE. The formal potential of the 1,4-benzoquinone couple is -0.96V relative to the ferrocene\(^{+1/0}\) couple in CH\(_2\)Cl\(_2\) (a larger difference than reported, -0.85V, in acetonitrile\(^{24} \)). Voltammetry was taken of 0.5 mM solutions of \( \text{Au}_{38}(\text{SC}2\text{PhS})_{24} \) (in CH\(_2\)Cl\(_2\) /50 mM Bu\(_4\)NPF\(_6\)) to which one to five equivalents (relative to the MPC cores) of triphenylphosphine were added, allowing at least 3 hours for completion of the reaction.

UV-vis spectra of CH\(_2\)Cl\(_2\) solutions were collected with a Shimadzu UV-vis (Model UV-1601) spectrometer. \(^1\)H, \(^{31}\)P and \(^{13}\)C NMR spectra were collected on a Bruker 500 MHz
DRX spectrometer. Reaction kinetics were examined by collecting $^1$H NMR spectra at 293K from well-mixed CD$_2$Cl$_2$ solutions of MPC (~1 mM) and PPh$_3$ at timed intervals of 10 or 20 minutes. For lowered temperature kinetics, CD$_2$Cl$_2$ solutions of MPC and PPh$_3$ were chilled by liquid N$_2$, the temperature of the inner NMR probe was adjusted to 253K and stabilized, and the chilled solutions were mixed in an NMR tube which was placed in the NMR probe. 10 to 15 minutes were required for mixing the reactants, thermal equilibration of the NMR tube in the probe and NMR parameter setup. Reaction time was counted from the instant of mixing. When desired, the CD$_2$Cl$_2$ reactant solutions were degassed separately, mixed under argon, and the reaction mixture transferred to an Ar-filled NMR tube sealed with a vacuum tight rubber cap.

3.3 Results and Discussion

3.3.1 UV-Vis Spectroscopy.

Figure 3.1a shows the UV-Vis spectrum of Au$_{38}$(SC2Ph)$_{24}$ in CH$_2$Cl$_2$, which has a step-like structure with bands at ca. 681, 444 and 400 nm. A few hours after mixing the Au$_{38}$(SC2Ph)$_{24}$ solution (~1 mM) with 20 equivalents PPh$_3$ (i.e., a mole ratio of PPh$_3$ over cluster core of 20, which is about one PPh$_3$ for each thiolate ligand), the solution color has changed from dark red to light yellow, the spectral fine structure due to Au$_{38}$(SC2Ph)$_{24}$ has been lost, and after 24 hours, a new band at ca. 420 nm has emerged. The product from this reaction (with excess PPh$_3$) is soluble in methanol, whereas the original Au$_{38}$(SC2Ph)$_{24}$ MPC was methanol-insoluble. Figure 3.1b shows spectra after 3 hour reactions of Au$_{38}$(SC2Ph)$_{24}$ with smaller amounts of added PPh$_3$. Reactions with less than 5 equivalents of PPh$_3$
preserve the Au$_{38}$(SC2Ph)$_{24}$ spectral features although they become less distinct. A reaction with 10 equivalents gives the same result as in Figure 3.1a.

The spectral changes in Figure 3.1 qualitatively show that PPh$_3$ is quite reactive toward the thiolate-protected Au MPC. The reaction could be a simple replacement of thiolate with PPh$_3$, or a more complex process leading to a change in the MPC core size. The Figure 3.1 results suggest the latter. Thiolate-protected MPCs with larger cores generally exhibit a smoothly increasing absorbance from the visible to UV region, and for cores > 2 nm diameter, a surface plasmon band emerges at about 520 nm.$^{7b,25}$ These characteristics are quite unlike the 24 hour spectrum in Figure 3.1a, which instead is roughly similar to spectra of smaller-sized undecagold clusters.$^{14b,20,26}$ The similarity hints that the reaction of Au$_{38}$(SC2Ph)$_{24}$ with a 20-fold molar excess of PPh$_3$ leads to a new MPC with a smaller core size.

There is precedent for a decrease in core size when MPCs are exposed to excesses of other ligands. Whetten et al.$^{27}$ described the “etching” of thiolate-protected noble metal nanocrystals by alkanethiols and Hicks et al.$^{28}$ described “annealing” of 1.6 nm Au MPCs to improve core size monodispersity. These reports speculated on the role of Au$^I$(thiolate) complexes as a vector for migration of Au atoms. Likewise, core size change was noticed in reactions of Au$_{11}$(PPh$_3$)$_8$Cl$_3$ with large excesses of thiols. Even without added ligands, PPh$_3$-capped Au clusters (for example, Au$_{55}$(PPh$_3$)$_{12}$Cl$_6$) are not stable in solution and undergo decomposition.$^{19}$

**3.3.2 $^1$H and $^{31}$P NMR.**

NMR experiments provide more direct evidence of the nature of the PPh$_3$/MPC
Figure 3.1 (a) UV-Vis spectra of PPh$_3$, Au$_{38}$(SC2Ph)$_{24}$, and of a 20:1 mole ratio mixture of PPh$_3$ and Au$_{38}$(SC2Ph)$_{24}$, after reacting in dichloromethane for 3.5 and 24 hours, respectively. (b) The UV-Vis spectra of mixtures of PPh$_3$ and Au$_{38}$(SC2Ph)$_{24}$ in mole ratios of 2:1, 5:1, and 10:1 after reacting in dichloromethane for 3 hours. For comparison, the absorbances are normalized at 300 nm. Au$_{38}$(SC2Ph)$_{24}$ concentration is ca. 1 mM.
(a) $\text{PPh}_3$, $\text{Au}_{38}(\text{PhC}_2)_24$, $\text{Au}_{38}(\text{PhC}_2)_24 + \text{PPh}_3$ (x20), 3.5 hours

(b) $\text{Au}_{38}(\text{PhC}_2)_24$, $\text{Au}_{38}(\text{PhC}_2)_24 + \text{PPh}_3$ (x2), 3 hours

Absorbance (a. u.)

Wavelength /nm
reactions. In these experiments, the added PPh$_3$ was limited to 1 to 5 equivalents per Au$_{38}$(SC$_2$Ph)$_{24}$ cluster. The immediate reaction products were not isolated but rather observed in the CD$_2$Cl$_2$ solution reaction mixtures.

The methylene region of $^1$H NMR spectra (Figure 3.2) is the most informative regarding the reaction between Au$_{38}$(SC$_2$Ph)$_{24}$ and PPh$_3$. Figure 3.2a shows the spectrum of the Au MPC,Au$_{38}$(SC$_2$Ph)$_{24}$, which has been reported before.$^{7b}$ The methylenes of the -SC$_2$Ph ligands exhibit three peaks (labeled as C1 C2, C3 in Ref. 21) at 2.95, 3.1, and 3.6 ppm; the different ligand environments that these represent has not been unraveled. The Au$_{38}$(SC$_2$Ph)$_{24}$ spectrum also contains resonances for the phenyl group at about 7.2 ppm (Figure 3.3a). The intensity$^{7b}$ ratio of the phenyl peaks to the summed methylene peaks is 1.32, close to the expected 1.25.

Figure 3.2b shows the $^1$H NMR of a 1:1.9 mole:mole mixture of Au$_{38}$(SC$_2$Ph)$_{24}$ and PPh$_3$ after a three hour reaction period (no further change occurs at longer times). A notable effect, compared to Figure 3.2a, is the appearance of two new peaks at ca. 3.0 and 3.2 ppm (triplets). At lowered temperature (Figure 3.2c), the 3.0 and 3.2 ppm multiplets remain sharply defined while the other resonances become broadened in the manner expected for slowed rotation diffusion of the nanoparticle. This result is consistent with the 3.0 and 3.2 ppm resonances representing a species no longer attached to the nanoparticle. The chemical shifts of the clearly methylene resonances at 3.0 and 3.2 ppm do not however, correspond at all to any of the more obvious possibilities of phenylethylene-S- moieties released by displacement of a thiolate ligand from the MPC core by PPh$_3$, such as thiol (Figure 3.2e), disulfide (Figure 3.2f), or thiolate (Figure 3.2g). In contrast to this result, ligand exchanges between thiols and thiolate-protected MPC liberate the thiolate ligands as free thiols, as has
Figure 3.2  Methylene resonances (ppm) of phenylethanethiol in $^1$H NMR of room temperature solutions of a) ~1 mM Au$_{38}$(SC2Ph)$_{24}$, b) 1:1.9 mole:mole mixture of Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$ after 3 hours, c) same as (b) except at 253 K and 1:3 mole ratio, d) Au$_4$SC2Ph complex, e) phenylethanethiol, f) (PhC2S)$_2$ disulfide produced by iodine oxidation of phenylethanethiol, and g) PhC2S$^-$ thiolate produced by reacting phenylethanethiol with 1 equivalent of Bu$_4$N$^+$OH$^-$. In e-g) the multiplets at about 2.80 and 2.95 ppm are S-CH2 and CH2-phenyl, respectively. In a), b), d) the –NCH$_2$- of Oct$_4$N$^+$ impurity overlaps with and may enhance the 3.1 ppm peak.
(a) $\text{Au}_{38}(\text{PhC}_2)_{24}$

(b) $\text{Au}_{38}(\text{PhC}_2)_{24} \cdot \text{PPh}_3$ (1:1.9)

(c) $\text{Au}_{38}(\text{PhC}_2)_{24} \cdot \text{PPh}_3$ (1:3), 253 K

(d) $\text{Au}^\ddagger\text{SC}_2\text{Ph}$

(e) $\text{HSC}_2\text{Ph}$

(f) $(\text{SC}_2\text{Ph})_2$

(g) $\cdot \text{SC}_2\text{Ph}$
Figure 3.3  Aromatic resonances (ppm) of $^1$H NMR of room temperature solutions of a) ~1 mM Au$_{38}$(SC$_2$Ph)$_{24}$, b) 1:1.9 mole:mole mixture of Au$_{38}$(SC$_2$Ph)$_{24}$ and PPh$_3$ after 3 hours, c) same as (b) except at 253 K and 1:3 mole ratio, d) Au$^1$SC$_2$Ph complex, e) phenylethanethiol, f) (PhC$_2$S)$_2$ disulfide produced by iodine oxidation of phenylethanethiol, and g) PhC$_2$S$^-$ thiolate produced by reacting phenylethanethiol with 1 equivalent of Bu$_4$N$^+$OH$^-$, h) free PPh$_3$.

# The aromatic hydrogen atoms from OPPh$_3$ impurity (in the PPh$_3$) in $^1$H NMR spectrum have chemical shifts of 7.5~7.7 ppm which partially overlap those from bonded PPh$_3$ (7.4~7.7 ppm) but are separated from those from free PPh$_3$ (7.3~7.4 ppm).$^{29}$
(a) \( \text{Au}_{38}(\text{PhC}_2)_{24} \)

(b) \( \text{Au}_{38}(\text{PhC}_2)_{24}^+\text{PPh}_3 \)

(c) \( \text{Au}_{38}(\text{PhC}_2)_{24}^+\text{PPh}_3 \)

(d) \( \text{Au}^{1}\text{SC}_2\text{Ph} \)

(e) \( \text{HSC}_2\text{Ph} \)

(f) \( \text{(SC}_2\text{Ph)}_2 \)

(g) \( \text{HSC}_2\text{Ph} \)

(h) \( \text{PPh}_3 \)
been established from $^1$H NMR observations.$^{46,10}$

Figure 3.2d shows the $^1$H NMR spectrum of a solution of Au$^{1}$SC2Ph complex prepared as in Experimental. It is known that Au$^{1}$-thiolate complexes, possibly partially polymerized, are formed as intermediates during the Brust synthesis of MPCs.$^6$ Isolating and drying such complexes results in a white insoluble solid (unless the thiolate is a bulky group$^{23}$), whereas it remains partially soluble if not dried and used fresh. The Au$^{1}$SC2Ph complex prepared (as a saturated solution—even then the concentration was low) for the Figure 3.2d experiment displays three methylene peak multiplets centered at 3.0, 3.2, and 3.6 ppm (with phenyl/methylene intensity ratio of 1.26; the ideal is 1.25). The former two multiplets match the new resonances seen in Figure 3.2b following reaction between Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$. This observation indicates that the Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$ reaction results in the release of the original thiolate ligand from the Au core as Au$^{1}$SC2Ph complexes. The released complexes seem to not be polymeric, judging from their simpler spectra at 3.0 and 3.2 ppm, and because a dried Au$_{38}$(SC2Ph)$_{24}$/PPh$_3$ reaction mixture can be completely redissolved.

The above assessment is supported by $^{13}$C NMR spectra (see Figure 3.4), where in a Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$ reaction mixture, additional peaks (*) for SC2Ph appear, compared to the $^{13}$C NMR spectrum of Au$_{38}$(SC2Ph)$_{24}$. The chemical shift of the new peak at 36 ppm that is assigned to the C1 carbon (-S-CH$_2$-) differs from that in PhC2SH and (PhC2S)$_2$ (see Figure 3.4 and Table 3.1a). The downfield shift of the C1 resonance is consistent with adjacency to an electron withdrawing group (i.e., Au$^1$). The $^{13}$C chemical shift assignment for C1 agreed with the $^{13}$C NMR spectra of Au$^1$-(4-tert-butylnbenzyl mercaptan)$^{23}$ where the same downfield shift (38 ppm) appears for -CH$_2$-S- in a prepared Au$^1$SC2Ph complex,
Table 3.1 (a) $^{13}$C chemical shifts from a 1:3 mixture of $\text{Au}_{38}(\text{PhC}_2)_{24}$ and PPh$_3$, and of PhC2SH and of (PhC2S)$_2$ in $\text{CD}_2\text{Cl}_2$. (The chemical shifts of $\alpha$-C and m-C were overlapped by features from PPh$_3$ and are not listed in the table.) (b) Chemical shifts from $^{13}$C NMR of $\text{Au}^1$(4-<i>tert</i>-butylbenzyl mercaptan) and 4-<i>tert</i>-butylbenzyl mercaptan and its disulfide. See Figure 3.4.
<table>
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<tr>
<th></th>
<th>C-p (Ph-)</th>
<th>C-i (Ph-)</th>
<th>C2 (-CH2-)</th>
<th>C1(-CH2-)</th>
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</thead>
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<tr>
<td>Au$<em>{38}$(PhC2)$</em>{24}$ /PPh$_3$ mixture</td>
<td>140.8</td>
<td>127.0</td>
<td>41.0</td>
<td>36.2</td>
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<tr>
<td>PhC2SH</td>
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<td>126.8</td>
<td>40.6</td>
<td>26.5</td>
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<tr>
<td>(PhC2S)$_2$</td>
<td>140.0</td>
<td>126.8</td>
<td>40.0</td>
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</table>

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<tr>
<th></th>
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<th>C-b</th>
<th>C-c</th>
<th>C-d</th>
<th>C-e</th>
<th>C-f</th>
<th>C-g</th>
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<tr>
<td>Au$^1$-SR</td>
<td>38.3</td>
<td>139.7</td>
<td>129.4</td>
<td>125.8</td>
<td>150.1</td>
<td>34.7</td>
<td>31.4</td>
</tr>
<tr>
<td>H-SR</td>
<td>28.8</td>
<td>138.8</td>
<td>128.1</td>
<td>125.9</td>
<td>150.3</td>
<td>34.8</td>
<td>31.6</td>
</tr>
</tbody>
</table>
Table 3.2 Results from reaction between $\text{Au}_{38}(\text{SC2Ph})_{24}$ and $\text{PPh}_3$ in $\text{CD}_2\text{Cl}_2$ under various conditions.
<table>
<thead>
<tr>
<th>Reaction Condition</th>
<th>293 K, Air</th>
<th>253 K, Air</th>
<th>293 K, Argon</th>
<th>293 K, Air, Acetic acid $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[PPh$<em>3$]$</em>{\text{ADDED}}$/[Au MPC]$_{\text{INIT}}$ $^a$</td>
<td>1.9</td>
<td>3.0</td>
<td>2.6</td>
<td>3.0</td>
</tr>
<tr>
<td>[Au$^1$SC2Ph]/[Au MPC]$_{\text{INIT}}$ $^b$</td>
<td>1.8</td>
<td>2.8</td>
<td>2.5</td>
<td>____ $^e$</td>
</tr>
<tr>
<td>([PPh$<em>3$]$</em>{\text{ISOLAT}}$/[Au MPC]) $^c$</td>
<td>0.7</td>
<td>2.0</td>
<td>1.1</td>
<td>2.2</td>
</tr>
<tr>
<td>pseudo-first-order rate constant ($k_{OBs}$), s$^{-1}$</td>
<td>____</td>
<td>2.3 x 10$^{-4}$</td>
<td>9.3 x 10$^{-5}$</td>
<td>____</td>
</tr>
<tr>
<td>second-order rate constant ($k_{EX}$), M$^{-1}$s$^{-1}$</td>
<td>____</td>
<td>8.5 x 10$^{-2}$</td>
<td>4.0 x 10$^{-2}$</td>
<td>____</td>
</tr>
<tr>
<td>$k_{EX}$ (comparison only $^g$), M$^{-1}$s$^{-1}$</td>
<td>____</td>
<td>2.1 x 10$^{-3}$</td>
<td>8.3 x 10$^{-4}$</td>
<td>____</td>
</tr>
</tbody>
</table>

a) Mole:mole ratio of PPh$_3$ to Au MPCs in the reaction; [Au MPCs] is always 0.93 mM. The change in PPh$_3$ by generation of impurity OPPh$_3$ has been corrected.$^{29}$
b) Based on integrated peak area in $^1$H NMR at 3.2 ppm for methylene groups of Au$^1$SC2Ph in mixtures of Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$ relative to integrated peak area around 7.2 ppm for phenyl groups in spectra of Au$_{38}$(SC2Ph)$_{24}$ MPCs, prior to mixing with PPh$_3$. The methyl resonance of Oct$_4$N$^+$ impurity at 0.9 ppm was taken as internal standard in the two solutions.
c) Based on $^1$H NMR of iodine-decomposed Au MPCs after methanol purification of exchange reaction product. The numbers of Au atoms and ligands per MPC are assumed to remain at 38 and 24, respectively, although results on the loss Au$^1$SC2Ph complexes indicate both may be less by perhaps 10%.
d) Acetic acid added in 1:1 mole:mole relative to triphenylphosphine.
e) Integration of the Au$^1$SC2Ph peak at 3.2 ppm in $^1$H NMR was not possible owing to the overlapping broad peak of the MPC in acid solution (see Figure 3.5).
f) Calculated from $k_{OBs}$ and [PPh$_3$]$_{\text{ADDED}}$ by assuming a second-order process$^{4f,10}$.
g) Assuming the initial concentration of PPh$_3$ equal to that of incoming p-substituted arylthiols ($\sim$5:1, incoming ligand: PhC2) in thiolated-ligand exchange reaction with Au$_{38}$(PhC2)$_{24}$.$^{10l}$
Figure 3.4 $^1$H-decoupled $^{13}$C NMR (in CD$_2$Cl$_2$) of (a) 1.1 nm Au MPCs after reacting with 3.0 equivalent moles of PPh$_3$ (* designates $^{13}$C resonances from Au$^1$PhC2), (b) Au$_{38}$(PhC2)$_{24}$, (c) PPh3, (d) tetraoctylammonium bromide (TOABr), (e) PhC2SH, and (f) (PhC2S)$_2$ (from reaction of PhC2SH and iodine).
(a) Au$_{38}$(PhC$_2$)$_{24}$ + PPh$_3$ (1:3)

(b) Au$_{38}$(PhC$_2$)$_{24}$

(c) PPh$_3$

(d) TOABr

(e) PhC$_2$SH

(f) (PhC$_2$)$_2$
Figure 3.5 $^1$H-decoupled $^{13}$C NMR (in CD$_2$Cl$_2$) of (a) Au$^1$-(4-tert-butylbenzyl mercaptan), (b) 4-tert-butylbenzyl mercaptan, and (c) disulfide of 4-tert-butylbenzyl mercaptan (from reaction of 4-tert-butylbenzyl mercaptan and iodine).
(a) Au(I)-SR

(b) H-SR

(c) RS-SR

PPM
relative to 27 ppm for C1 in the free parent thiol 4-tert-butylbenzyl mercaptan and its disulfide (see Figure 3.5 and Table 3.1b). The shifted C1 $^{13}$C resonance in the Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$ reaction mixture is evidence of a Au$^1$SC2Ph complex there as well.

The quantity of released Au$^1$SC2Ph complexes was assessed from the intensity of the methylene triplet at 3.2 ppm in spectra like Figure 3.2b, relative to that of the integrated phenyl resonances at about 7.1-7.2 ppm in the $^1$H NMR spectrum of Au$_{38}$(PhC2)$_{24}$ (before mixing with PPh$_3$). The latter measures the five phenyl protons on MPC-bond SC2Ph thiolates, which is proportional to the initial concentration of Au MPCs. The results in Table 3.2, second line, show that the resulting ratio $[\text{Au}^1\text{SC2Ph}]/[\text{Au MPC}]_{\text{INIT}} = 1.8$ quantitatively equals the 1.9 mole ratio of the reactants, $[\text{PPh}_3]_{\text{ADDED}}/[\text{Au MPC}]_{\text{INIT}}$. The concentration ratios were also equal (Table 3.2) for reactions conducted at reduced temperature or under Ar. The clear inference is that, at low $[\text{PPh}_3]_{\text{ADDED}}/[\text{Au MPC}]_{\text{INIT}}$ mole ratios, the reaction between Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$ has a 1:1 stoichiometry and goes to completion.

Resonances in the 7-8 ppm aromatic region (Figure 3.3) are also consistent with the above analysis of the methylene region. The phenylethane multiplets in the spectrum for Au$_{38}$(SC2Ph)$_{24}$ MPC, for the Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$ reaction mixture, and Au$^1$SC2Ph complexes all lie at about 7.1-7.2 ppm (Figure 3.3a,b,c, respectively), whereas those for phenylethanethiol itself and its disulfide and free thiolate lie between 7.2 and 7.3 ppm and are not consistent with Figure 3.3b. The phenyl resonances for PPh$_3$ in the spectrum of the Au$_{38}$(SC2Ph)$_{24}$ and PPh$_3$ reaction mixture lie between 7.4 and 7.7 ppm (Figure 3.3b), whereas those for free PPh$_3$ ligand lie between 7.3 and 7.4 ppm (Figure 3.3h). The 7.3-7.4 ppm PPh$_3$ interval in the reaction mixture Figure 3.3b shows very little intensity, supporting the conclusion from Table 3.1, that reaction between Au$_{38}$(SC2Ph)$_{24}$ and small excess of
PPh₃ proceeds to completion. Completeness of reaction is additionally supported by the absence of a peak at the -4.3 ppm chemical shift known for free PPh₃ in a ³¹P NMR spectrum of the reaction mixture. Instead the ³¹P NMR spectrum of a Au₃⁸(SC₂Ph)₂⁴/PPh₃ reaction mixture (Figure 3.6) exhibits a single PPh₃ peak at 39.5 ppm that, relative to the sharp resonance of impurity triphenylphosphine oxide (OPPh₃, 29.3 ppm), is substantially broadened. Both the chemical shift change and peak broadening (an effect seen before for PPh₃ bonded to Au₁₀₁ clusters and interpreted as fast dissociative exchange with free PPh₃) are consistent with the PPh₃ ligand being bonded to the Au MPCs.

MPC reaction product from reactions between Au₃⁸(SC₂Ph)₂⁴ and PPh₃ (1~5 equivalent moles) was isolated from the solution by addition of methanol, followed by thorough washing of the precipitate with methanol. The ¹H NMR spectrum of this product (Figure 3.7a) was broadened relative to that seen in the reaction mixture before isolation, and its UV-Vis spectrum (Figure 3.8) was less sharply defined relative to spectra of the reaction solution prior to isolation (Figure 3.1). The monolayer shell of the isolated product was analyzed by decomposing the MPC with iodine and measuring the relative numbers of liberated ligands by ¹H NMR (Figure 3.7b). The results (Table 3.1) show that the number of PPh₃ ligands per MPC in the isolated product ([PPh₃]_{ISOLAT}/[Au MPC]) is smaller than the reaction ratio [PPh₃]_{ADDED}/[Au MPC]_{INIT}.

The preceding results on release of Au(SC₂Ph) complex upon reaction of, for example, a 1:3 mole:mole ratio Au₃⁸(SC₂Ph)₂⁴ and PPh₃, mean that the core atom count becomes decreased by three, while at the same time replacing the original phenylethylthiolate ligands with PPh₃ ligands that are substantially more bulky and labile.²ᵃ,¹⁷,¹⁸ᵇ,²⁰ It is thus unsurprising that PPh₃ ligands are dissociatively lost during the isolation and methanol washing of the reaction.
Figure 3.6  $^{31}\text{P}$ NMR of a 1:2.6 mole:mole mixture of Au$_{38}$(SC$_2$Ph)$_{24}$ and PPh$_3$ in CD$_2$Cl$_2$ at room temperature. The inset is a full spectrum.
Figure 3.7 (a) $^1$H NMR of 1.1 nm MPCs after reacting with 3.0 equivalent moles of PPh$_3$ in CH$_2$Cl$_2$ and purified with MeOH; (b) $^1$H NMR of iodine-decomposed MPCs as described above. The mole ratio of PPh$_3$ over PhC$_2$ was given by the ratio of integrated peaks area at 7.52 ppm (phenyl groups in Au(I)-PPh$_3$) over that at 7.3 ppm (phenyl group in PhC$_2$) or 2.9 ppm (ethylene group in PhC$_2$).
product. Table 3.1 suggests that loss of as many as two of three PPh₃ ligands bound during the reaction could occur. Some additional loss of thiolate ligands might conceivably also occur owing the steric requirements of PPh₃ and as a result of partial loss of the stable Au₃₈ closed shell core structure. Finally, there are many known or postulated reasons for broadened NMR spectra of MPCs, including nanoparticle poly-dispersity, diversity of chemical shifts around the MPC core, and dispersity of ligand solvation or motional freedom around the core. Since the core size is changed by the reaction with PPh₃, any of these reasons might provoke the changes in NMR and UV-Vis spectra in Figure 3.8 and 3.7a. No further analysis of the changed, isolated product was attempted.

3.3.3 Reaction Kinetics: Effect of Temperature and Oxygen.

Figure 3.9 depicts the extent of reaction between Au₃₈(SC₂Ph)₂₄ and PPh₃ as a function of time under different conditions, determined as detailed in the figure caption. At room temperature and in air, the reaction is so fast that equilibrium is reached in minutes. The reaction is slowed at lower temperature. The kinetics during the initial stage of reaction were analyzed as a pseudo-first-order process with rate constant \( k_{OBS} = k_{EX}[\text{PPh}_3]_{ADDED} \) by plotting the fraction of not-yet-reacted Au₃₈(PhC₂)₂₄ versus time, as shown in the inset of Figure 3.9. The pseudo-first-order rate constants \( k_{OBS} \), as well as second-order rate constants \( k_{EX} \) calculated assuming a second order process, are listed in Table 3.1. Rui et al. studied thiolate-for-thiolate ligand exchange kinetics on Au₃₈(PhC₂)₂₄ clusters with different \( p \)-substituted arylthiols in CD₂Cl₂ at 293K. The resulting second-order rate constants were between \( 2.3 \times 10^{-3} \) and \( 1.0 \times 10^{-2} \) M⁻¹s⁻¹, depending on the substituent. The exchange reaction between PPh₃ and Au₃₈(PhC₂)₂₄ is clearly faster than that between this
Figure 3.8 UV-Vis spectra of $\text{Au}_{38}$(PhC2)$_{24}$ (black) and isolated Au clusters (blue) from the 3:1 mol/mol reaction between PPh$_3$ and $\text{Au}_{38}$(PhC2)$_{24}$ in CH$_2$Cl$_2$. 
**Wavelength /nm**

400 600 800 1000

**Normalized Absorbance**

0.0 0.2 0.4 0.6 0.8 1.0

**Au$_{38}$(PhC2)$_{24}$**

**Isolated Au clusters**
Figure 3.9 Kinetics results, based on analysis of $^1$H NMR spectra, from reaction between PPh$_3$ and ~1 mM Au$_{38}$(SC$_2$Ph)$_{24}$ at 293 K in air (●), at 253 K in air (▲), and at 293 K in argon (■). Reaction extent is defined as the ratio of instant concentration of Au$^1$SC$_2$Ph released from the reaction over equilibrium concentration of Au$^1$SC$_2$Ph after the reaction and is given by the corresponding ratio of integrated triplet peak areas at 3.2 ppm in $^1$H NMR of the reaction mixture of PPh$_3$ and Au$_{38}$(SC$_2$Ph)$_{24}$. The inset is a plot of ln $Y$ ($Y = [Au_{38}(SC_2Ph)_{24}]_{TIME}/[Au_{38}(PhC2)_{24}]_{INIT}$) versus time for exchange reaction of Au$_{38}$(PhC2)$_{24}$ at 253K in air. The slope gives pseudo-first-order rate constant for the reaction.
Reaction Extent /%

0 10 20 30 40 50 60 70 80 90 100 110

Time /min

0 50 100 150 200 250 300

lnY

Slope\(=-k_{\text{obs}}=-1.37 \times 10^{-2}/\text{min}\)

\(r^2=0.97\)

293K, Air
253K, Air
293K, Argon

Inset:

Time /min

0 25 50 75 100

lnY

-1.5
-2.0
-2.5

253K, Air
MPC and ρ-substituted arylthiols, by about an order of magnitude, even though the rates of the former are somewhat depressed by having been determined at lower temperature and in absence of oxygen. The fast exchange reaction rate is consistent with the observation of rapid phosphine exchange on intermediate-size or larger Au clusters on which the phosphine replacement has a half-life from 1-2 minutes to milliseconds.\textsuperscript{10b,15-18}

Figure 3.9 also illustrates the decelerating effect on the kinetics, of excluding dioxygen from the reaction mixture. The effect of oxygen is presumably as an oxidant toward Au\textsubscript{38}, facilitating the formation of Au\textsuperscript{1}-thiol,\textsuperscript{34} the product of exchange reaction. The same effect was found in thiolate-for-thiolate ligand exchange reactions,\textsuperscript{10k} which are also accelerated by positive charges on the Au MPC core.

### 3.3.4 Comments on the Reaction Mechanism.

A reaction of PPh\textsubscript{3} with Au\textsubscript{38}(PhC\textsubscript{2})\textsubscript{24} that results in replacement of a negatively charged thiolate ligand by a neutral PPh\textsubscript{3} creates a charge imbalance that can be accommodated either by leaving the Au positively charged, or by departure of positive charge from the core such as in a Au\textsuperscript{1} complex. The NMR evidence above is persuasive that the latter occurs, concurrently effecting a decrease in the MPC core atom count. Based on the NMR observations, the reaction between Au\textsubscript{38}(SC2Ph)\textsubscript{24} MPCs and PPh\textsubscript{3} is proposed as, showing the first two reaction steps,

\begin{equation}
Au_{38}(SC2Ph)_{24} + PPh_{3} \longrightarrow Au_{37}(SC2Ph)_{23}(PPh_{3}) + [Au(1)SC2Ph] \tag{1}
\end{equation}

\begin{equation}
Au_{37}(SC2Ph)_{23}(PPh_{3}) + PPh_{3} \rightarrow Au_{36}(SC2Ph)_{22}(PPh_{3})_{2} + [Au(I)SC6Ph] \tag{2}
\end{equation}

These reactions are based on the NMR evidence (Figure 3.2) that the thiolate released from the Au\textsubscript{38}(SC2Ph)\textsubscript{24} MPC upon reaction with PPh\textsubscript{3} is as a Au\textsuperscript{1} complex, as opposed to as a
thiol, disulfide, or thiolate. For small numbers of reacting PPh$_3$ ligands, the release of Au$^1$SC$_2$Ph, and consumption of PPh$_3$, has a 1:1 stoichiometry and is quantitative. The diminution of the atom count in the nanoparticle core, by successive losses of Au, at some point destabilizes the core; the evidence suggests that this occurs between 5 and 10 reaction steps. The UV-Vis spectral changes imply that the nanoparticles may be reorganized into a more stable Au$_{11}$ moiety, but the spectral evidence for that is far from conclusive.

Reactions 1, 2, etc., are not ligand “exchanges”, and thus differ from reactions of thiols with thiolate-protected Au MPCs that result (except when conducted in the presence of large excesses of thiols) in core size retention.$^{10}$ In a study of Au$_{38}$(SC$_2$Ph)$_{24}$ MPCs, for example, it was possible to exhaustively replace the phenylethylthiolate ligands with $p$-X-phenylethylthiolates, and then in a second exchange, to replace the $p$-X-phenylethylthiolates with phenylethylthiolates, without loss of Au$_{38}$ core integrity.$^{10l}$ Thiolate-for-thiolate exchanges have 1:1 stoichiometry, are substantially associative as opposed to dissociative reactions,$^{10k,l}$ and yield the displaced ligand as a thiol. Au$^1$(thiolate) complexes are not thought to be involved in the associative reaction, but under oxidizing conditions (air, positive core change) demonstrably can act as a vector for transferring Au from MPC to MPC and across solvent phase boundaries.$^{10k}$

What are the reason(s) for the substantial difference between thiolate-for-thiolate and phosphine-for-thiolate reactions? Given the general lability of phosphine ligands on Au nanoparticles, as compared to thiolate ligands, and the thermodynamic stability of Au-thiolate bonding,$^{35}$ it is somewhat surprising that the phosphine-for-thiolate reaction occurs so readily. One is led to speculate that some aspect of Au-thiolate chemistry may provide an important reaction-driving factor, possibly the stability of Au$^1$SC$_2$Ph complexes. Use of an
acid medium to stabilize leaving thiolate ligands does not seem to provide a comparable stabilization; reacting 3:1 mole:mole PPh$_3$ with Au$_{38}$(SC$_2$Ph)$_{24}$ in the presence of a concentration of acetic acid equal to that of the PPh$_3$ apparently did not alter the course of the reaction (Table 3.1, Figure 3.5).

3.3.5 In Situ Electrochemistry

Differential pulse voltammetry (DPV) of Au$_{38}$ clusters before and after mixing with varied amounts of PPh$_3$ is shown in Figure 3.10. The voltammetry of the molecule-like Au$_{38}$(SC$_2$Ph)$_{24}$ MPC has been described previously.$^{21}$ Table 3.3 shows how the potential spacing between the indicated waves changes as a function of different relative amounts of PPh$_3$, letting the reaction run to completion. Table 3.4 shows how the spacing between the first two oxidation steps $\Delta E^o_{+2/+1,+1/0}$ and the solution rest potentials change as a function of reaction time. The spacing $\Delta E^o_{+2/+1,+1/0}$ reflects the degree to which solvation and screening in the CH$_2$Cl$_2$ solution stabilize increased positive charge on the MPC core; we have referred$^{21}$ to it as the charging energy.

Several facts are obvious from the electrochemical data: 1) While the basic features$^{21}$ of Au$_{38}$(PhC$_2$)$_{24}$ voltammetry remain recognizable during the reaction, new oxidation peaks appear, a sign of changes in the energies of electronic states of the reaction products. 2) Additionally, the second oxidation peak becomes modestly irreversible.$^{36}$ It is unsurprising that electrochemical (positive) charging of the PPh$_3$-capped Au clusters makes them less stable. A more positive Au core charge should facilitate the departure of Au$^1$-thiolate complexes. The leaving of the Au$^1$ complex lessens the positive charge on the core of the nanoparticle, i.e., is somewhat equivalent to reducing it. This speculation is supported by the
**Table 3.3** Electrochemical study of PPh$_3$ reaction with Au$_{38}$(SC$_2$Ph)$_{24}$ as a function of relative amount of PPh$_3$. Formal potentials are averages of potentials of current peaks in positive and negative-going scans in DPVs taken at 20mV/s. Voltammetry was done in CH$_2$Cl$_2$ with 1.6 mm diameter gold working electrode; potentials are referenced to the reduction of 1,4-benzoquinone (BQ) to its radical anion.
<table>
<thead>
<tr>
<th>$n_{\text{PPh}_3}$ / mol</th>
<th>$\Delta E^o_{+1/0, -1/0}$</th>
<th>$\Delta E^o_{+2/+1, +1/0}$</th>
<th>$\Delta E^o_{+3/+2, +2/+1}$</th>
<th>$[\Delta E^o_{+1/0, -1/0}]$</th>
<th>$-[\Delta E^o_{+2/+1, +1/0}]$</th>
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</tr>
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<td>1.652</td>
<td>0.296</td>
<td>/</td>
<td>1.356</td>
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</tr>
</tbody>
</table>
Table 3.4 In situ electrochemical detection of reaction between Au$_{38}$(PhC2)$_{24}$ and PPh$_3$ (3-fold molar excess) in CH$_2$Cl$_2$ with added acetic acid (one equivalent mole relative to the amount of PPh$_3$) (left) or without acetic acid (right) as a function of reaction time. Listed are rest potentials and peak spacing between first two DPV oxidation waves.
<table>
<thead>
<tr>
<th>Time /min</th>
<th>$\Delta E^{\circ}_{+2/+1,+1/0}$ mV vs BQ</th>
<th>$E_{\text{Rest}}$ mV vs BQ</th>
<th>Time /min</th>
<th>$\Delta E^{\circ}_{+2/+1,+1/0}$ mV vs BQ</th>
<th>$E_{\text{Rest}}$ mV vs BQ</th>
</tr>
</thead>
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<td>336</td>
<td>-107</td>
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<td>-120</td>
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</table>
Figure 3.10 Differential pulse voltammetry of $\text{Au}_{38}(\text{SC2Ph})_{24}$ (a) and a mixture of $\text{PPh}_3$ and $\text{Au}_{38}(\text{SC2Ph})_{24}$ in mole ratio of 3:1 (b) and 6:1 (c) after 3 hours reaction at room temperature. All voltammetry was done in $\text{CH}_2\text{Cl}_2$ with 1.6 mm diameter gold working electrode. 1,4-Benzoquinone (BQ) is taken as internal reference (this couple is -0.96 vs. ferrocene in $\text{CH}_2\text{Cl}_2$). The peak with asterisk is associated with the residual dioxygen that was not completely removed by Ar degassing.
observation (Table 3.4) that the rest potential of the MPC solution (reflecting the Fermi level of the core) shifts negatively as PPh$_3$ added (and Au$^1$ complex is lost). Alternatively one may say that a polar Au-S bond on the MPC is replaced with a less polar Au-P bond. 3) The reaction is rapid, most of the change in $\Delta E^o_{+2/+1,+1/0}$ (which indirectly reflects changes in the nanoparticle) happens in the first ten minutes (consistent with the Figure 3.9 $^1$H NMR observations). 4) The electrochemical HOMO-LUMO energy gap (highest occupied molecular orbital to lowest unoccupied molecular orbital) is estimated as the difference $\{[\Delta E^o_{+1/0,-1/0}]-[\Delta E^o_{+2/+1,+1/0}]\}$, where the second term represents our estimate$^{21,37}$ of the work term (“charging energy”) associated with charging the nanoparticle to -1 or +1. The HOMO-LUMO gap decreases slightly first and then increases continuously as more and more PPh$_3$ exchanged onto the Au core.

Understanding the small changes in the HOMO-LUMO energy gap (Table 3.3) is complicated by the likelihood that the gap depends on both change in core size and the capping ligands. Smaller core MPCs are known$^{38}$ to exhibit a larger energy gap, whereas n-dodecanethiolate-protected undecagold clusters are reported to have a gap energy of 1.76 eV as compared to a smaller gap energy, 1.41 eV, for Au$_{11}$Cl$_3$(PPh$_3$)$_7$. It is possible that these two opposing effects cause the behavior in Table 3.3. Additionally, Table 3.3 shows that small changes in $\Delta E^o_{+2/+1,+1/0}$ also occur, and using this quantity for estimation of the charging energy may lead to artificial bias in the HOMO-LUMO energy gap. What can be said is that the small size of the overall gap change resulting, at say $n_{PPh3} = 6$ is quite modest considering that the core is presumably now Au$_{32}$ and six thiolate ligands have been ousted by PPh$_3$ bonding.
References:


26. The UV-Vis spectrum of undecagold clusters $^{14b, 20}$, either PPh$_3$ capped or thiolate-ligand protected, show an absorbance around 416 nm, which is coincident with the absorbance peak at 410 nm in Graph 1 (x20 PPh$_3$ added).


29. Solutions of PPh$_3$ exposed to the air always contain some OPPh$_3$ impurity, whose amount can be estimated in $^1$H NMR spectra based on its aromatic proton resonances (7.5~7.7 ppm) relative to those of PPh$_3$ (7.3~7.4 ppm).


35. From a thermodynamic viewpoint, Au-S bonding ($D_{298}^{298}$=418 kJ/mol)$^{14a}$ is proposed to be stronger than Au-P. $^{13, 14b}$
36. DPV of Au$_{38}$(SC2Ph)$_{24}$ reacted with > 10 equivalent moles of PPh$_3$ show ill-defined features beyond the first oxidation wave and a large current peak at negative potentials.


CHAPTER IV

ELECTRON TRANSFER DYNAMICS IN A ROOM TEMPERATURE AU NANOPARTICLE MOLTEN SALT


4.1 Introduction

Our previous studies of highly-concentrated redox moieties in viscous, amorphous media have focused on a basic understanding of their electrochemistry and electron transfer dynamics, which would play a role in their application as energy storage materials.1 A variety of chemical materials—from metal complexes2 to organic entities3 to DNA4—have been transformed into room temperature amorphous molten salts by judicious covalent attachments of poly(ethylene) glycol (PEG) oligomers, to for example metal complex ligands (e.g., bipyridine2, tetraphenylporphyrin5) or to their counterions6,3b. This route to generation of molecular melts has proved to be completely general, and works by disrupting normally crystalline structures with dis-ordered PEG appendages, forming glassy or semi-solid media consisting of concentrated redox sites diluted only modestly by the PEG component. In the electrochemical reactions of these media, as examined by microelectrode methodologies,7 the combination of high redox site concentrations and their very slow physical diffusivities
engenders electron transport by electron hopping. These have proved to be excellent model media for study of electron transport in semi-solid, localized redox site materials.  

Our initial analysis of electron transport in redox melts focused on a solvent dynamics interpretation.  

Evidence for the coupling of electron transport to counterion mobility extends over a wide range of PEG-based molten salts.  

For example, for cobalt and ruthenium complex molten salts, the results demonstrate (a) a 1:1 proportionality between counterion diffusion coefficient and both heterogeneous (e.g. Co(III/II)) and homogeneous (e.g. Co(II/I)) electron transfer rates, (b) very similar thermal energy barriers for electron transfer and counterion diffusion, and (c) electron transfer rates fall to effectively zero when the counterion (e.g., DNA) is immobile. Substantial effort has been put into structural variations of metal complex molten salts in terms of metals (Co, Ru), counterions (ClO₄⁻ or I⁻)
PEG linkage (to cation or anion), number of PEG chains, supporting electrolyte addition and CO₂ plasticization. All of these examples have entailed more or less conventional redox materials, and all have shown adherence to the ionic relaxation analysis. It is with interest in exploring the *generality* of ionic atmosphere relaxation in electron hopping transport that in this chapter, we turn to less conventional redox reactions, namely electron transfer between molecule-like Au nanoparticles.

This chapter describes molten salts based on 1.1 nm diameter Au₃₈ thiolate monolayer-protected nanoparticles. These nanoparticles are part of a family of nanoparticles within which over a 1-3 nm range of core diameters, properties change from those of bulk Au (or at least Au particles that lack a homo-lumo energy gap) to those which exhibit such a gap. The Au₃₈ nanoparticles, or monolayer-protected clusters (MPCs), with phenylethanthiolate ligand monolayers and an estimated Au₃₈(PhC₂)₂₄ formula, display in dilute dichloromethane solutions cleanly-defined voltammetric one-electron oxidation and reduction transformations that are separated by 1.6 V. After correction for charging energy, the estimated homo-lumo gap energy is *ca.* 1.33 eV, which is confirmed by optical band edge measurement. While this molecule-like behavior justifies treatment as a redox moiety, electron transfer dynamics between tiny clumps of metal atoms remains a novel area of chemistry.

The above-mentioned energy gap properties are preserved upon exchange of some of the original phenylethyl thiolate ligands with thiolated PEG ligands. Our tactic to prepare a molecular melt of Au₃₈ nanoparticles relies on the successful melt-generation ideas noted above, of attaching poly(ethylene) glycol chains. In this case, the poly(ethylene) glycol chains attached as thiolate ligands produce a highly viscous, room temperature melt in which
the melt components are PEGylated nanoparticles as illustrated in Figure 4.1. Electrolyte (LiClO₄) is dissolved in the nanoparticle phase (much as in a polymer electrolyte) along with some unattached PEG to make the melt ionically conductive enough to allow microelectrode voltammetry in the undiluted material. The PEGylated ligand, -S-C₆-PEGₕ₃₅ (single compound, 3 ethylene oxide repeat units), used in Figure 4.1 differs from that used previously by Lee and Donkers et al. who synthesized PEG₃₅₀ (mixture of oligomers, 7.2 ethylene oxide repeat units on average) thiolate-ligand protected Au₃₈. The present inclusion of the hexane segment and use of a shorter PEG chain improved the free ligand’s solubility in heptane, facilitating its cleanup.

The electron hopping dynamics between Au₃₈⁰ and Au₃₈¹⁺ nanoparticles and the mass transport properties of electrolyte ions were studied at room temperature and below in the resulting Au₃₈ nanoparticle melts. The electron hopping dynamics were measured by potential step chronoamperometry of the Au₃₈⁺¹/₀ voltammetric wave; the electron diffusion coefficient (Dₑ) is converted to apparent electron self-exchange rate constants (kₑₓ). Ionic conductivities were measured by ac impedance and converted to physical diffusion coefficients of perchlorate ions (Dᶜ⁻) with the Nernst-Einstein relation. The thermal activation barrier energies of each were obtained by varying temperatures. Further manipulation of overall melt fluidity, and of transport rates, as accomplished by plasticization by sorption of high pressure CO₂. These measurements follow those used previously.

The resulting values of Dₑ and of Dᶜ⁻ vary in a 1:1 manner, and their thermal barrier energies are very similar. These results show that ion atmosphere relaxation can control the effective rate of electron transport in a semi-solid nanoparticle phase, just as it does in the well-studied metal complex molten salts.
Figure 4.1 A cartoon of the structure of $\text{Au}_{38}(\text{PhC2})_{15}(\text{SC6PEG}_{163})_9$. 
4.2 Experimental

Chemicals. All chemicals were reagent grade and used as received if not otherwise stated. Poly(ethylene glycol) methyl ether (MW 350 and 550) was dried in a vacuum oven at 75°C for at least 3 days before use. \( \text{Au}_{38}(\text{PhC}2)_{24} \) nanoparticles were prepared as described before.\(^{12a}\)

Syntheses. The PEGylated thiol (1-mercaptohex-6-yl)tri(ethylene glycol) methyl ether (HS-C6-PEG\(_{163}\)) was prepared by procedures similar to that reported by Whitesides et al.\(^{16}\)

Hex-1-en-6-yltri(ethylene glycol) methyl ether. A mixture of 0.79 mL of 50% aqueous sodium hydroxide (10 mmol) and 1.5 g of tri(ethylene glycol) monomethyl ether (9.1 mmol) was stirred for 30 min. in an oil bath at 100°C under Ar, and then 2.98 g of 6-bromohex-1-ene (18.3 mmol) was added. After 24 hours, the reaction mixture was cooled and extracted six times with hexane. Combining and rotary evaporation of the combined hexane portions at reduced pressure gave a colorless oil whose content of un-reacted 6-bromohex-1-ene was removed by silica gel chromatography with serial elutions by hexane (500mL), 25% (v/v) ethyl acetate in hexane (400 mL) and acetone (300 mL). The hex-1-en-6-yltri(ethylene glycol) product in the ethyl acetate-hexane mixture was proved by \( ^1 \text{H NMR in CD}_2\text{Cl}_2 \) (5.32 ppm): \( \delta \) 1.42 (qui, 2 H), 1.55 (qui, 2 H), 2.05 (q, 2H), 3.32 (s, 3 H), 3.42 (t, 2 H), 3.48-3.65 (m, 12 H), 4.90-5.05 (m, 2 H), 5.75-5.88 (m, 1 H).

[1-[(Methylcarbonyl)thio]hex-6-yl]tri(ethylene glycol) methyl ether. Solutions of the above olefin (350 mg, 1.42mmol) in THF (8 mL) containing thiolacetic acid (1.06 mL, 14.2 mmol) and 30 mg of AIBN (0.183 mmol) were irradiated for 24 hours under Ar with a 450-W medium pressure mercury lamp (Ace Glass). The reaction mixture was concentrated by rotary evaporation at reduced pressure and purified by silica gel chromatography (400 ml
CH₂Cl₂ followed by 200 mL 10% CH₃OH in CH₂Cl₂), giving the thioacetate as confirmed by
¹H NMR in CD₂Cl₂ (5.32 ppm): δ 1.35 (m, 4 H), 1.55 (m, 4 H), 2.3 (s, 3 H), 2.84 (t, 2 H),
3.32 (s, 3 H), 3.42 (t, 2 H), 3.48-3.65 (m, 12 H).

(1-Mercaptohex-6-yl)tri(ethylene glycol) methyl ether. The thioacetate (360 mg, 0.58
mmol) was refluxed for 6 hours in 0.1 M HCl in methanol under Ar. The reaction mixture
was extracted into CH₂Cl₂ (20 mL, twice) and washed with saturated aq. KHCO₃ (20 mL,
thrice) and then pure water (20 mL, thrice), and dried using sodium sulfate, which was
filtrated off. Concentrating the solution by rotary evaporation gave the PEGylated thiol HS-
C₆-PEG₁₆₃, as confirmed by ¹H NMR in CD₂Cl₂ (5.32 ppm): δ 1.35 (m, 4 H), 1.55 (m, 4 H),
2.50 (q, 2 H), 3.32 (s, 3 H), 3.42 (t, 2 H), 3.48-3.65 (m, 12 H).

Preparation of PEGylated Au₃₈ Melts. HS-C₆-PEG₁₆₃ was incorporated into the
monolayer of Au₃₈ nanoparticles by ligand exchange. In a typical procedure, 17 mg of
Au₃₈(PhC₂)₂₄ was stirred in the dark with 3 equivalent moles of HS-C₆-PEG₁₆₃ (32 mg) in 10
mL methylene chloride for 24 hours. Concentrating the reaction mixture by rotary
evaporation gave a dark-red oil which was washed several times with n-heptane to remove
free thiol as evidenced by the absence of their α-thiol proton resonances in ¹H NMR. The
relative proportion of PEGylated and PhC₂ thiolates in the resulting mixed monolayer was
determined by decomposing the Au₃₈ nanoparticle with a crystal of iodine, analyzing the
liberated mixture of disulfides¹⁷ by ¹H NMR.

Free methyl-terminated PEG (MW = 350 or 550) plasticizer and LiClO₄ electrolyte
were added to the resulted mixed monolayer Au₃₈(PhC₂)₁₅(SC₆PEG₁₆₃)₉ melt by dissolving
all in acetonitrile¹⁸, mixing thoroughly, and evaporating the solvent. PEG plasticizers were
added in at least 5:1 molar chain proportions, relative to the -SC₆PEG₁₆₃ ligands, and LiClO₄
electrolyte was added at a 1:16 mole ratio of Li$^+$ over ether oxygen as usual, which is about 1M concentration in the dried melt.$^{9b,27}$

**Measurements.** $^1$H NMR were collected on a Bruker 500 MHz DRX Spectrometer and referenced to deuteron-methylene chloride (D, 99.9%, Cambridge Isotope Laboratories, Inc.)

Voltammetry in dilute CH$_2$Cl$_2$ or CH$_3$CN solutions (with 0.1 M Bu$_4$NPF$_6$ electrolyte) and in undiluted polyether melts of nanoparticles was done with a CHI 660A Electrochemical Workstation. Voltammetry in degassed dilute solutions used a 1.6 mm diameter Pt disk working electrode, and Ag wire quasi-reference and Pt coil counter electrodes. Voltammetry was executed on films of Au$_{38}$ polyether melts with added LiClO$_4$ on a polished, insulating platform in which tips of two Pt (12.5 µm radius as working and 0.4 mm diameter as counter electrode) and one Ag (0.5 mm diameter quasi-reference electrode) wires were exposed. A second 0.4 mm diameter Pt wire tip was also present in the platform and was used with the other 0.4 mm tip during ionic conductivity measurements. The platform was polished with successively smaller grades (down to 0.05 µm) of alumina and the Pt tips electrochemically cleaned by cycling in 0.1 M H$_2$SO$_4$. The film of nanoparticle melt was drop-cast onto the electrode platform to a thickness at about 1 mm and dried in vacuo ($ca.$ 1x10$^{-3}$ Torr) for 24 hours. The electrochemistry was also performed in vacuo, and the films and cell enclosure were pre-equilibrated at each temperature and pressure for at least 2 hours. Chronoamperometric potential steps (300 to 500 mV) were guided by initial cyclic voltammetric scans and started in a non-Faradaic region just before the Au$_{38}^{+1/0}$ wave to a diffusion limited potential past the Au$_{38}^{+1/0}$ peak (but short of the Au$_{38}^{+2/+1}$ reaction). The current-time results were analyzed by the Cottrell equation.$^7$
Ionic conductivities of nanoparticle melts (with added LiClO₄) were measured by ac impedance using a Solartron Model SI 1260 impedance/gain phase analyzer-SI 1287 electrochemical interface combination, over a 1-500 kHz frequency range, at 0 V dc bias and 50 mV amplitude. Ionic conductivity was calculated as the ratio of geometric cell constant (calibrated by standard solutions) and cell resistance taken from the low frequency real-axis intercept of the complex impedance semicircle.

4.3 Results and Discussion

4.3.1 Ligand Exchange.

The nanoparticle melts used here have been prepared by ligand exchanges of the PEGylated thiol HS-C6-PEG₁₆₃ with the well-characterized \( \text{Au}_{38}(\text{PhC}_2)_{24} \). It is of course important that the \( \text{Au}_{38} \) core remain intact through the exchange procedure. This has been shown to be the case for \( \text{Au}_{38} \) in other studies and confirming electrochemical and spectral evidence is presented next.

Figure 4.2 compares dilute solution differential pulse voltammetry (DPV) of the ligand exchanged product, \( \text{Au}_{38}(\text{PhC}_2)_{15}(\text{SC6PEG}_1\text{63})_9 \), with that of the original nanoparticle \( \text{Au}_{38}(\text{PhC}_2)_{24} \). The pattern of redox changes for \( \text{Au}_{38}(\text{PhC}_2)_{24} \) has been discussed previously, the current peaks at \( \text{ca.} +0.1 \text{ V vs. QRE} \) represent loss of the first electron from the \( \text{Au}_{38} \) core whereas those at \( \text{ca.} -1.5 \text{ V} \) represent the first reduction step of the core. The difference between their potentials, \( E_{\text{APP, GAP}} \), represents the HOMO-LUMO energy gap plus charging energy. The charging energy is approximated by the difference in potential for loss of the first and second electrons (\( \Delta E^{+2/+1,+1/0} \)). These data are listed in Table 4.1 for \( \text{Au}_{38}(\text{PhC}_2)_{15}(\text{SC6PEG}_1\text{63})_9 \) and \( \text{Au}_{38}(\text{PhC}_2)_{24} \) and for two other reported mixed monolayer
Au_{38} examples.\textsuperscript{12} It is seen that the general appearance of the Figure 4.2 voltammetry, and the numerical results for Au_{38}(PhC2)_{15}(SC6PEG_{163})_{9} of $E_{\text{APP,GAP}}$ and HOMO-LUMO energy gap, 1.65 and 1.34 V, respectively, are nearly identical to those of Au_{38}(PhC2)_{24} and the other nanoparticles. The small differences seen could be due to a combination of experimental uncertainty and differences between electronic inductive effects\textsuperscript{13} of the different ligands.

The UV-Vis spectra of Au_{38}(PhC2)_{15}(SC6PEG_{163})_{9} and Au_{38}(PhC2)_{24} solutions (Figure 4.3) are also nearly identical; three absorbance features appear in each case at 400 nm, 445 nm, and 680 nm, along with other minor inflections.\textsuperscript{12a} The absorbance coefficients differ to a small degree; that of Au_{38}(PhC2)_{15}(SC6PEG_{163})_{9} is about 10\% larger at 680 nm for example. Other data on Au_{38} nanoparticles also show small increases in absorbance coefficient as the monolayer becomes increasingly PEGylated.\textsuperscript{21} Overall, neither the electronic spectra or voltammetry of the PEGylated Au_{38}(PhC2)_{15}(SC6PEG_{163})_{9} become significantly altered. Assuming that these properties are influenced by the nanoparticle core size, the results indicate that core size changes do not occur.

### 4.3.2 Electron Charge Transport and Counterion Transport

The oxidative cyclic voltammetry of a Au_{38}(PhC2)_{15}(SC6PEG_{163})_{9} melt containing MePEG plasticizer and 1 M LiClO\textsubscript{4} electrolyte is shown in Figure 4.4a at room temperature and in Figure 4.4b at a series of temperatures. The melt exhibits a series of oxidative features similar to those in dilute solution (Figure 4.2), except that the product of the third oxidation step is apparently unstable, with following chemical events leading to further electron transfer steps. The +1/0 and +2/+1 waves are better behaved; the former appears to
Table 4.1 Comparison of formal potentials (E vs. QRE) and spacing between waves (V) of various oxidation and reduction states of \( \text{Au}_{38}(\text{PhC2})_{24} \), \( \text{Au}_{38}(\text{PhC2})_{15}(\text{SC6PEG})_{9} \), \( \text{Au}_{38}(\text{PhC2})_{11}(\text{SPEG})_{13} \) and \( \text{Au}_{38}(\text{C6S})_{22}(\text{PhC2S})_{2} \) in methylene chloride containing 0.1 M \( \text{Bu}_4\text{NPF}_6 \).
<table>
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<th>Nanoparticle \ Potential, V</th>
<th>$\Delta E^o_{+3/+2, +2/+1}$</th>
<th>$\Delta E^o_{+2/+1, +1/0}$</th>
<th>$\Delta E^o_{+1/0, -1/0}$</th>
<th>$[\Delta E^o_{+1/0, -1/0}]_{b}^{a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$<em>{38}$(PhC2)$</em>{24}$</td>
<td>0.74</td>
<td>0.29</td>
<td>1.62</td>
<td>1.33</td>
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<tr>
<td>Au$<em>{38}$(PhC2)$</em>{15}$(SC6PEG$_{163}$)$_9$</td>
<td>0.77</td>
<td>0.31</td>
<td>1.65</td>
<td>1.34</td>
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<td>Au$<em>{38}$(PhC2)$</em>{11}$(SPEG$<em>{135}$)$</em>{13}$</td>
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<td>0.26</td>
<td>1.65</td>
<td>1.39</td>
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<tr>
<td>Au$<em>{38}$(C6S)$</em>{22}$(PhC2S)$_2$</td>
<td>0.80</td>
<td>0.34</td>
<td>1.68</td>
<td>1.34</td>
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</tbody>
</table>

a. $\Delta E^o_{+3/+2, +2/+1} = E^o_{+3/+2} - E^o_{+2/+1}$, difference between first and second formal oxidation potentials.

b. Electrochemical HOMO-LUMO gap after the charging energy correction.
Figure 4.2 Differential pulse voltammograms (DPVs) of (a) $\text{Au}_{38}\text{(PhC}_2\text{)}_{24}$ in methylene chloride and (b) of $\text{Au}_{38}\text{(PhC}_2\text{)}_{15}\text{(SC}_6\text{PEG163})_9$ in acetonitrile with 0.1 M $\text{Bu}_4\text{NPF}_6$ as supporting electrolyte, at 1.6 mm diameter Pt disk working electrode. DC Potential scan rate = 0.02 V/s. The star indicates currents from residual dioxygen.
\[ \Delta E^o \]

(a) \[ \Delta E^o \]

(b) \[ \Delta E^o \]

\[ E_{APP, GAP} \]

Potential vs. AgQRE (V)
Figure 4.3  Comparison of UV-Vis spectra of $\text{Au}_{38}(\text{PhC}2)_{15}(\text{SC6PEG163})_9$ (black) and $\text{Au}_{38}(\text{PhC}2)_{24}$ (red) in methylene chloride. Absorbance coefficients at 680 nm are given for comparison.
Wavelength / nm

<table>
<thead>
<tr>
<th>200</th>
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<th>800</th>
<th>1000</th>
<th>1200</th>
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<td>4</td>
<td>6</td>
<td>8</td>
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<td>12</td>
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</tbody>
</table>

Absorbance coefficient / M⁻¹cm⁻¹

<table>
<thead>
<tr>
<th>Au₃₈(PhC₂)₂₄</th>
<th>ε₆₈₀nm=1.31x10⁴ M⁻¹cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au₃₈(PhC₂)₁₅(SC₆PEG₁₆₃)₉</td>
<td>ε₆₈₀nm=1.46x10⁴ M⁻¹cm⁻¹</td>
</tr>
</tbody>
</table>

445 nm
400 nm
680 nm
be cleanly chemically reversible. The shape of the voltammetric waves indicates linear transport geometry—even though a microelectrode is employed—because of the very slow transport rates. Without the added plasticizer, the uncompensated resistance is sufficiently large as to significantly distort the voltammetry; the $iR_{UNC}$ effect even with MePEG plasticizer present is substantial. Figure 4.4b shows that the peak currents for the $\text{Au}_{38}^{1+/0}$ reaction increase with temperature from $-10^\circ\text{C}$ to $20^\circ\text{C}$, as expected for an increase in diffusive charge transport rates. We note that although the currents are larger at higher temperature, the $iR_{UNC}$ effect is smaller ($\Delta E_{\text{PEAK}}$ between oxidation and reduction peak currents decreases); this is because while the currents increase with the square root of charge transport $D_{\text{APP}}$, while solution resistance scales inversely linearly with $D_{\text{APP}}$. At the highest temperature shown ($30^\circ\text{C}$), the reduction return wave seems smaller, suggesting an onset of thermal instability. Temperatures used for transport measurements were accordingly kept below $25^\circ\text{C}$.

The rates of electron transport in nanoparticle melts containing different proportions of MePEG plasticizer were measured by chronoamperometry, stepping the potential over the first $\text{Au}_{38}$ oxidation peak. In the concentrated, highly viscous melt, the apparent charge transport diffusion coefficient ($D_{\text{APP}}$) is expected to be a summation of the coefficients for physical diffusion ($D_{\text{PHYS}}$) of the $\text{Au}_{38}(\text{PhC2})_{15}(\text{SC6PEG}_{163})_9$ moiety and for electron diffusion ($D_E$) by hopping between $\text{Au}_{38}^0$ and $\text{Au}_{38}^{+1}$ centers in the mixed valent transport layer formed around the working electrode. The pertinent relation is known as the Dahms-Ruff equation, $^{22}$ and the value of $D_E$ is connected to the electron self-exchange rate constant ($k_{\text{EX}}$) with a cubic lattice model: $^{22}$

$$D_{\text{APP}} = D_{\text{PHYS}} + D_E = D_{\text{PHYS}} + \frac{k_{\text{EX}} \delta^2 C}{6}$$

(1)
Figure 4.4 Cyclic voltammetry at 25 mV/sec of Au$_{38}$ polyether melts with added MePEG$_{350}$ (5:1) and 1 M LiClO$_4$ (Li$^+$:ether oxygen≈1:16) on 12.5 µm Pt disk microelectrode. (a) The positive-going scan variously stops beyond first (−), second (—) and third oxidation peak (--), respectively. The temperature is at 25°C. (b) The scan stops beyond the first oxidation peak, and temperatures are varied from -10°C to 30°C.
Potential vs. AgQRE (V)

Current (A)

(a)

(b)

Potential vs. AgQRE (V)
where $\delta$ is the average equilibrium center-to-center distance between Au$_{38}$ sites and $C$ is the total concentration of redox sites.

Our experience with polyether-based molecular melts and molten salts has been that the rates of physical diffusion of bulky redox centers in the highly viscous, semi-solid media are usually much smaller than $D_E$; i.e., $D_{\text{APP}} \approx D_E^{2.8}$. In metal complex polyether melts, for example, $D_{\text{PHYS}}$ of the PEGylated complex $[\text{Co(bpy(MePEG$_{350}$)$_2$)$_3$}]^{2+}$ is $\text{ca. } 10^{-11}$ cm$^2$sec$^{-1}$, but $D_E$ for electron hopping between $[\text{Co(bpy(MePEG$_{350}$)$_2$)$_3$}]^{2+}$ and $[\text{Co(bpy(MePEG$_{350}$)$_2$)$_3$}]^{1+}$ is about two orders of magnitude larger.$^{8a}$ The apparent diffusion coefficient measured is therefore dominated by $D_E$ with negligible contribution from $D_{\text{PHYS}}$. In those melts, the value of $D_{\text{PHYS}}$ was measured from currents for the $[\text{Co(bpy(MePEG$_{350}$)$_2$)$_3$}]^{3+/2+}$ oxidation wave. We followed a similar strategy in the nanoparticle melts, using a dilute solution of $[\text{Co(bpy(MePEG$_{350}$)$_2$)$_3$}]^{2+}$ in the nanoparticle melt (the metal complex and Au$_{38}$ nanoparticle have roughly the same dimensions) as a surrogate for a non-electron hopping Au$_{38}$ (in this case reducing the Co complex rather than oxidizing it).

As shown in Figure 4.5, A semi-quantitative comparison of diffusion coefficients based on peak current of Co(II/I) and Au$_{38}$(+1/0) is feasible. The reduction peak current of Co(II/I) is $\text{ca. } 1 \times 10^{-10}$ A in 23% mixture; the peak current for Au$_{38}$(+1/0) is $\text{ca. } 1.2 \times 10^{-9}$ A in the 9% mixture. Converting the relative peak currents into relative diffusion coefficients, remembering that peak current is proportional to $D^{1/2}$, the above data show that $D_{\text{Co(II/I)}}$ is only $\sim 7\%$ of $D_{\text{Au38(+1/0)}}$. Considering that diluting the Au$_{38}$ nanoparticle melt with the Co melt would somewhat depress the electron hopping between Au$_{38}$ sites, and that the assumption of no electron hopping between the Co complex may not be totally true, the real difference between reduction current of Au$_{38}$(+1/0) and that of Co(II/I) can be even larger. This
analysis suggests that physical diffusion is indeed much smaller than electron diffusion in the 
Au$_{38}$ nanoparticle melt, and can be reasonably ignored within insignificant error. The 
electron self-exchange rate constants ($k_{EX}$) were accordingly calculated directly from $D_{APP}$. 
The results are shown in Table 4.2. As expected the charge transport rates increase with 
added plasticizer. The results will be discussed further below.

Sorption of CO$_2$ at high pressure is another useful tactic to systematically$^{8a,b}$ 
manipulate melt fluidity to examine responses of transport rates. Sorption and the presumed 
increase in internal free volume has been found to enhance both electron hopping and 
counterion transport to degrees dependent on the CO$_2$ pressure.$^{23}$ Cyclic voltammetry of the 
Au$_{38}$ nanoparticle melt at 25°C is shown in Figure 4.6 under different CO$_2$ pressures. The 
peak currents increase with pressure, as expected, but at 400 psi there is a significant change 
of peak shape and an enhanced return reduction wave, suggesting that transport of oxidized 
Au$_{38}$ states away from the electrode interface has somehow been greatly slowed. Higher 
pressures were accordingly not employed. Charge transport rates in the CO$_2$-plasticized 
melts were measured using chronoamperometry, and the $k_{EX}$ results$^{24}$ (again taking $D_{APP} \approx$ 
$D_e$) are given in Table 4.3. The charge transport rates for both Me-PEG and CO$_2$-plasticized 
Au$_{38}$ nanoparticle melts were also measured over a range of temperatures; the thermal 
activation plots are shown in Figure 4.7 and the barrier energies ($E_{A,ET}$) are found in Tables 
4.2 and 4.3.

The rates of counterion transport in Me-PEG and CO$_2$-plasticized Au$_{38}$ nanoparticle 
melts, containing ca. 1 M LiClO$_4$, were evaluated from ionic conductivity measurements 
($\sigma_{ION}$) using the Nernst-Einstein equation as done previously,$^{9b,25}$

$$\sigma_{ION} = \frac{F^2}{RT} \left[ z_{Li^+}^2 D_{Li^+} C_{Li^+} + z_{ClO_4^-}^2 D_{ClO_4^-} C_{ClO_4^-} \right]$$  \hspace{1cm} (2)
Table 4.2 Transport data (25°C) from voltammetric measurements of electron transfer rate and conductivity measurements of ion diffusion in Au_{38} nanoparticle polyether melt with added plasticizer MePEG_{350} or MePEG_{550} and LiClO_{4} electrolyte (in most cases, Li^{+}:ether oxygen≈1:16) \textsuperscript{9b,27}. 
<table>
<thead>
<tr>
<th>Measured parameter / plasticizer content&lt;sup&gt;a&lt;/sup&gt;</th>
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<th>350</th>
<th>550</th>
<th>550</th>
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<td></td>
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<td>7.9:1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>5:1&lt;sup&gt;c&lt;/sup&gt;</td>
<td>5:1</td>
<td>10:1</td>
</tr>
<tr>
<td>$C_{\text{MPC}}^{d}/10^{-2}\text{M}$</td>
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<td>3.14</td>
<td>3.14</td>
<td>3.14</td>
<td>1.74</td>
</tr>
<tr>
<td>$C_{\text{LiClO}_4}^{e}/\text{M}$</td>
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<td>$C_{\text{ClO}<em>4^{-}}/C</em>{\text{MPC}}$</td>
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<td>37</td>
<td>9.2</td>
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<td>73</td>
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<tr>
<td>$d_{\text{core-to-core}}^{f}/\text{nm}$</td>
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<td>3.75</td>
<td>3.75</td>
<td>3.75</td>
<td>4.57</td>
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<td>$D_{\text{APP}} (25^\circ\text{C})/10^{6}\text{cm}^2\text{s}^{-1}$</td>
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<td>1.42</td>
<td>2.36</td>
<td>0.84</td>
<td>1.72</td>
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<tr>
<td>$k_{\text{EX}} (25^\circ\text{C})/10^7\text{M}^{-1}\text{s}^{-1}$</td>
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<td>1.92</td>
<td>3.50</td>
<td>1.15</td>
<td>2.84</td>
</tr>
<tr>
<td>$E_{\text{A,ET}}^{b}/\text{kJ mol}^{-1}$</td>
<td>54±1</td>
<td>49±3</td>
<td>----</td>
<td>50±1</td>
<td>63±4</td>
</tr>
<tr>
<td>$D_{\text{CION}}^{i} (25^\circ\text{C})/10^8\text{cm}^2\text{s}^{-1}$</td>
<td>1.19</td>
<td>1.84</td>
<td>1.73</td>
<td>1.86</td>
<td>1.83</td>
</tr>
<tr>
<td>$E_{\text{A, CION}}/\text{kJ mol}^{-1}$</td>
<td>54±2</td>
<td>53±4</td>
<td>----</td>
<td>56±4</td>
<td>53±1</td>
</tr>
<tr>
<td>$a/\text{nm (assuming } K_{eq}=1)$</td>
<td>2.68</td>
<td>2.74</td>
<td>----</td>
<td>3.56</td>
<td>3.02</td>
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<tr>
<td>$a/\text{nm (assuming } K_{eq}=0.1)$</td>
<td>0.85</td>
<td>0.87</td>
<td>----</td>
<td>1.13</td>
<td>0.96</td>
</tr>
</tbody>
</table>

<sup>a</sup> Plasticizer content is measured in ratio (e.g., 5:1) of moles added MePEG<sub>350</sub> relative to moles of -S-C6-PEG<sub>163</sub> ligands on Au<sub>38</sub>. All ratios in this row share the same meaning. <br><sup>b</sup> The total number of ethylene oxide groups of MePEG<sub>350</sub> (7.9:1) added is equivalent to that of MePEG<sub>550</sub> (5:1). <br><sup>c</sup> The melt with smaller amount of LiClO<sub>4</sub>. Li<sup>+</sup>:ether oxygen≈1:64. <br><sup>d</sup> The concentration is based on density measurements. <br><sup>e</sup> The actual mole concentration of LiClO<sub>4</sub>. <br><sup>f</sup> The average center-to-center distance is calculated by $d^3=1/(N_A C)$ assuming a cubic lattice model. <br><sup>g</sup> $D_{\text{PHYS}}$ was presumed negligible, compared to $D_{\text{E}}$. <br><sup>h</sup> From linear slopes of thermal activation plot of $k_{\text{EX}}$ (for data from 25°C to -10°C). <br><sup>i</sup> Thermal barrier values unavailable due to the strong curvature in Arrhenius plots (see Figure 4.11), an indication of coupled physical diffusion with segmental motions of PEG chains. $D_{\text{APP}}$ (or $k_{\text{EX}}$) may be overestimated due to the significant contribution from $D_{\text{PHYS}}$ in this case. <br><sup>j</sup> Calculated from conductivity according to Nernst-Einstein equation, assuming $D_{\text{Li}^+}=0$. 

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Figure 4.5 Cyclic voltammograms (25 mV/sec) of mixture of Au$_{38}$ polyether melts (91%, mol%) with added MePEG$_{550}$ (10:1) and 1 M LiClO$_4$ and [Co(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$](ClO$_4$)$_2$ (9%, mol%) on 12.5 µm Pt disk electrode at 25°C. The Co(II/I) reduction peak is almost invisible (9%, solid line) but can be distinguished at a higher Co mole concentration (23%, dotted line).
Potential (V)

Current (A)

9% Co + 91% Au$_{38}$

23% Co + 76% Au$_{38}$

Au$_{38}$ (+1/0)

Co(II/II)
where $z$, $D$, and $C$ are charge, diffusion coefficient, and concentration of the indicated species, respectively. Ionic conductivity in polymer electrolytes, and we assume also in the Au$_{38}$ nanoparticle melt, mainly reflects the physical mobility of the ClO$_4^-$ ion. Lithium ion transport in polyether solid electrolytes is known to be slowed by its interactions of PEG ether coordination sites. The diffusion coefficients of the perchlorate counterion ($D_{\text{ClO}_4}$, or $D_{\text{CION}}$) thusly calculated from ionic conductivities, and the thermal activation barrier energies for ion transport ($E_{A,\text{CION}}$) evaluated as in Figure 4.7, are listed in Tables 4.2 and 4.3.

### 4.3.3 Nature of Control of Au$_{38}^{1+/0}$ Electron Transfer Rate Constants

Inspection of the data in Tables 4.2 and 4.3 make obvious that both the rates of electron hopping transport ($D_{\text{APP}} \approx D_E$) and counterion transport ($D_{\text{CION}}$), as reflected in their respective diffusion coefficients, and their activation barrier energies ($E_{A,\text{ET}}$ and $E_{A,\text{CION}}$), are very similar in numerical magnitude and in variation with the degree of MePEG or CO$_2$-induced plasticization. The largest plasticization-induced changes are in the barrier energies in Table 4.3, but they remain the same for $E_{A,\text{ET}}$ and $E_{A,\text{CION}}$, and the $D_{\text{APP}}$ and $D_{\text{CION}}$ values remain similar. The correlations in these data are accentuated by the Figure 4.8(a,b) log-log plots of $k_{\text{EX}}$ and $D_{\text{CION}}$, where values of electron self-exchange rate constants linearly track their corresponding counterion diffusion coefficients, over different temperatures in melts plasticized with added MePEG$_{550}$ (5:1) and in room temperature melts plasticized at different CO$_2$ pressures. The slopes are near unity slope and the correlation extends over more than a 10-fold range. Tables 4.2 and 4.3 and Figure 4.8(a,b) strongly suggest that the rates of electron transfers between Au$_{38}^0$ and Au$_{38}^{+1}$ cores are closely-coupled to rates of counterion transport. It must be emphasized that the $D_E$ and $k_{\text{EX}}$ measurements are in a context of
Table 4.3 Transport data (25°C) from voltammetric measurements of electron transfer rate and conductivity measurements of counterion diffusion in Au$_{38}$ nanoparticle polyether melt with added MePEG$_{550}$ (5:1) and 1 M LiClO$_4$ ($\text{Li}^+:$ether oxygen$\approx$1:16).$^{9b}$
<table>
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<th>300</th>
<th>400</th>
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<tr>
<td>$D_{\text{APP}}$ (25°C) / $10^{-8}$ cm$^2$ s$^{-1}$</td>
<td>0.84</td>
<td>1.61</td>
<td>1.92</td>
<td>2.27</td>
<td>2.97</td>
</tr>
<tr>
<td>$k_{\text{EX}}$ (25°C) / $10^7$ M$^{-1}$ s$^{-1}$</td>
<td>1.15</td>
<td>2.38</td>
<td>2.84</td>
<td>3.37</td>
<td>4.40</td>
</tr>
<tr>
<td>$E_{\text{A, ET}}$ / kJ mol$^{-1}$</td>
<td>50</td>
<td>38</td>
<td>34</td>
<td>28</td>
<td>22</td>
</tr>
<tr>
<td>$D_{\text{CION}}$ (25°C) / $10^{-8}$ cm$^2$ s$^{-1}$</td>
<td>1.86</td>
<td>2.84</td>
<td>3.66</td>
<td>4.50</td>
<td>6.55</td>
</tr>
<tr>
<td>$E_{\text{A, CION}}$ / kJ mol$^{-1}$</td>
<td>56</td>
<td>43</td>
<td>38</td>
<td>34</td>
<td>24</td>
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</table>
Figure 4.6 Cyclic voltammograms (25 mV/sec) of Au$_{38}$ polyether melts with added MePEG$_{550}$ (5:1) and 1 M LiClO$_4$ (Li$^+$/ether oxygen\approx 1:16) on 12.5 µm Pt disk electrode at 15°C under vacuum and different CO$_2$ pressures.
Figure 4.7 Thermal activation plots for $D_{\text{CIOn}}$ and $D_{E}$ obtained in Au$_{38}$ nanoparticle melts with added MePEG$_{550}$ (5:1) and 1 M LiClO$_4$ over the temperature range of -10°C to 25°C in vacuum (●), and under CO$_2$ at 100 psi (■), 200 psi (▲), 300 psi (▼) and 400 psi (♦).
charge transport, that is, the rates obtained from $D_{\text{App}} \approx D_{E}$ are solely the rates of transfer events that are fruitful in conveying electronic charge to and from the working electrode in the nanoparticle melt.

Correlations like that in Figure 4.8 have been seen before, in the context of analogous charge and counterion transport investigations of polyether-based molten materials containing more conventional redox centers. Our analysis of the coupling between electron and counterion transport used a model termed ion atmosphere relaxation. The previous melts, and the $\text{Au}_{38}$ nanoparticle melts are highly viscous, amorphous media with high concentrations of electron donor-acceptor sites the ionically charged ones of which are intrinsically contact ion-paired with their counterions owing to the absence of any substantial diluting solvent. The electrostatic consequences of the strong ion association can be expected to be larger than would be the case in dilute solutions with excess electrolyte present and in which electrolyte ion mobility is furthermore much greater. The ion relaxation scheme is shown as a cartoon in Figure 4.9 and can be written

$$\text{ClO}_4^- \text{Au}_{38}^+ \text{Au}_{38}^0 \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} \text{ClO}_4^- \text{Au}_{38}^0 \text{Au}_{38}^+ \overset{k_2}{\rightarrow} \text{Au}_{38}^0 \text{Au}_{38}^+ \text{ClO}_4^-$$

where $k_1$ and $k_{-1}$ are the forward and reverse electron transfer rate constants and $k_2$ the rate constant for diffusive redistribution of the neighboring counterion(s). The counterion diffusion competes with the reverse electron transfer process; if it is slower (i.e., $k_2 \ll k_{-1}$) most of the forward electron transfers are followed simply by reverse electron transfer. The electrochemical measurement senses charge transport, and thus reflects only those events for which successful counterion relocation prevents back electron transfer. The counterion diffusion rate thus controls
Figure 4.8 (a) Linear log-log relationship between $k_{\text{EX}}$ and $D_{\text{ION}}$ for Au$_{38}^{+1/0}$ electron transport in polyether melts with added different amount of MePEG$_{350}$ or MePEG$_{550}$ over the temperature range of -10°C to 25°C in vacuum. The average slope is 1.02. (b) Linear log-log relationship between $k_{\text{EX}}$ and $D_{\text{ION}}$ for Au$_{38}^{+1/0}$ electron transfer in Au$_{38}$ polyether melts with added MePEG$_{550}$ (5:1) and 1 M LiClO$_4$ at a range of temperatures (-10°C to 25°C) in vacuum and different CO$_2$ pressure.
Figure 4.9  A cartoon of the electron transfer process controlled by counterion relaxation.
transport of electrons by the electron transfer reaction. The overall rate constant ($k_{EX}$) can be written as:

$$k_{EX} = \frac{k_1k_2}{k_2 + k_{-1}} \approx \frac{k_1k_2}{k_{-1}} = K_{EQ}k_2$$  \hspace{1cm} (3)

where $K_{EQ} = k_1/k_{-1}$. The rate constant ($k_2$) for diffusive counterion relocation rate constant can be modeled as:

$$k_2 = D_{CION} \left( \frac{\pi}{2a} \right)^2$$  \hspace{1cm} (4)

where $a$ is the diffusion distance.

Equations (3) and (4) leads the conclusion that the apparent electron transfer rate constant ($k_{EX}$) should be proportional to the counterion diffusion coefficient ($D_{CION}$), just as seen in Tables 4.2 and 4.3, and Figure 4.8.

No assumption is made in the above model regarding the chemical nature of the electron donor and acceptor sites, so the model’s potential is quite general. The measured electron transfer rate constants $k_{EX}$ are only apparent, not intrinsic values, being dominated by the slower rate of counterion diffusive relaxation to relieve the local charge imbalance. The generality of the ion atmosphere relaxation idea is emphasized by Figure 4.10, in which the Au$_{38}$ results are combined with analogous data from a variety of electron transfer reactions for other chemical species, including Co(II/I) bipyridine and phenanthroline complexes (PEGylated variously by attachment to the ligand or the counterion), Ru(III/II) bipyridine and cyano- complexes, and cobalticenium/cobaltocene. The intrinsic electron transfer rate constants for these disparate couples must surely span a wide range of different values, but in the context of their reactions in semi-solid melts that fruitfully yield electron
transport, they all fall onto a common correlation line (except the Ru cyano case which is the only non-spherically symmetrical example and which has been discussed\textsuperscript{8d}). The overall linear fitting gives an average slope of 1.00.

Let us finally examine the matter of the intercept of the correlated Au\textsubscript{38} melt data. The intercept according to Equations 3 and 4 contains the equilibrium constant $K_{\text{EQ}}$ and the diffusion distance $a$. Table 4.2 shows some calculations under different indicated assumptions. For an unselective reaction ($K_{\text{EQ}}$=1), the calculated diffusion length $a$ is smaller than the average center-to-center separation of the Au\textsubscript{38} nanoparticles. If $K_{\text{EQ}}$ is assumed to be less than unity (which is more reasonable given the unfavorable charge separation), $a$ is no more than a nanometer. These parameters suggest that the actual distance at which electron transfer occurs is smaller than the average center-to-center separation of the Au\textsubscript{38} nanoparticles, an analogous observation as in metal complex molten salts where electron transfer rates were independent of the attached polyether chain length.\textsuperscript{2c} The soft polyether shells certainly do not prevent neighboring Au nanoparticles from coming close to each other in a space defined by the organic components around the nanoparticles. It is unclear, however, to what extent the thermal motion of Au nanoparticles in the shells contributes to the energy barrier of electron transfer and how it is related to the dynamics of counterion relaxation.
Figure 4.10  The data in Figure 7 co-plotted with literature data from CO\textsubscript{2} plasticized melts, [Co(phen)\textsubscript{3}](MePEG\textsubscript{350}SO\textsubscript{3})\textsubscript{2} \textsuperscript{8b} (▽) and [Co(bpy(CO\textsubscript{2}MePEG\textsubscript{350})\textsubscript{2}]\textsubscript{3}[ClO\textsubscript{4}]\textsubscript{2} \textsuperscript{8a} (▼), MePEG\textsubscript{350} plasticized melt [Co(phen)\textsubscript{3}](MePEG\textsubscript{350}SO\textsubscript{3})\textsubscript{2} \textsuperscript{8c} in mole ratio of 6:1 (○), 3:1 (□) and 2:1 (△), and [Co(bpy(CO\textsubscript{2}MePEG\textsubscript{350})\textsubscript{2}]\textsubscript{3}(ClO\textsubscript{4})\textsubscript{2}+xLiClO\textsubscript{4} \textsubscript{9b} (■) (x=0~1.31), [Ru(bpy(CH\textsubscript{2}MePEG\textsubscript{350})\textsubscript{2}](CN)\textsubscript{2} plasticized with CO\textsubscript{2} (over a range of temperatures) \textsuperscript{8d} (●), [Ru(bpy(CO\textsubscript{2}MePEG\textsubscript{350})\textsubscript{2}]][X]\textsubscript{2}, where X=ClO\textsubscript{4}\textsuperscript{-} or a mixture of ClO\textsubscript{4}\textsuperscript{-} and I\textsuperscript{-} \textsuperscript{8e}, and [Cp\textsubscript{2}Co](MePEG\textsubscript{350}SO\textsubscript{3}) melt (neat, MePEG\textsubscript{350} plasticized or mixed with [FcTMA]\textsuperscript{+}) \textsuperscript{10} (▲). The overall slope for the linear correlation is 1.00.
Figure 4.11 Arrehius plot of $D_{\text{APP}}$ and $D_{\text{CION}}$ from the Au$_{38}$ nanoparticle molten salt with added MePEG$_{350}$ (5:1) and LiClO$_4$ (Li$^+$:ether oxygen$\approx$1:64). The strong curvature in Arrehius plot is due to the coupling between physical diffusion and segmental motions of PEG chains.
References and Notes


15. The Au$_{38}$ after ligand exchange reaction with PEGylate thiols is sparingly soluble in non-polar solvent (e.g., heptane).


18. PEGylated ligand protected Au$_{38}$ nanoparticles are soluble in a relatively polar solvent such as acetonitrile, in which Au$_{38}$(PhC$_2$)$_{24}$ is insoluble. The change of solubility is in part, evidence for the ligand exchange reaction.


24. The Table 4.3 data, and those given below for counterion transport in CO$_2$-plasticized melts, may underestimate the degree of transport enhancement since we were unable to ascertain the degree of melt swelling (and change in Au$_{38}$ concentration) caused by the CO$_2$ sorption. The unswollen concentration, 3.14x10$^{-2}$ M, was employed. Previously$^5a$ induced CO$_2$ swelling of a polyether-based metal complex melt was ca. 10% at 400 psi.


27. Previous study$^9b$ shows that the change in concentration of LiClO$_4$ has some complex effects on the fluidity (viscosity) of melts and the diffusivity of ions. The concurrent change of counterion concentration and diffusivity complicates the study of electron transfer dynamics. To maintain consistency of measurements, a constant ratio (1:16) of LiClO$_4$ and ethylene oxide repeat unit is taken as we did for various metal complex molten salts$^8d,12b$. 

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CHAPTER V
FERROCENATED IMIDAZOLIUMS: I. STRUCTURE AND PHYSICAL PROPERTIES

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5.1 Introduction

There has been an increasing growth of interest in the moisture-stable room-temperature ionic liquids (RTILs) based on the \(N,N'\)-dialkylimidazoliums since early 1990s.\(^1\)\(^2\) The RTILs offer unique physical and chemical properties,\(^2\) such as high thermal and chemical stability, negligible vapor pressure, and solubility of a wide range of organic and inorganic compounds, and as a promising solvent for a variety of applications such as organic synthesis,\(^3\) catalysis,\(^4\) separation,\(^5\) and photochemistry.\(^6\) More importantly, the inherent ionic conductivity and large potential window (~4V) of imidazolium ionic liquids make them attractive media for the fundamental study of novel electrochemical phenomena\(^7\) in such materials as well as applied electrochemical research in the areas of electrodeposition\(^8\), solar cells\(^9\), and electrical devices\(^10\).

Different from ILs based on dialkylimidazolium or other organic cations like \(N\)-alkylpyridinium or tetraalkylammonium, our laboratory has developed a strategy of forming ionic liquid phases by covalently-attaching low molecular weight poly(ethylene) glycol (PEG)
to redox species\textsuperscript{11-13} (e.g., metal complexes) or their counterions.\textsuperscript{14-15} This strategy proves to be such a general route that even liquid DNA \textsuperscript{11b} and a molten phase of sub-nanometer Au particles \textsuperscript{16} are successfully prepared for the purpose of electron transport studies. While all of our previous redox molten phases have been based solely on the incorporation of polyethers, it would be interesting to take advantage of structurally-different dialkylimidazoliums as the amorphous media, and to combine them with electroactive entities. This is further attractive considering other electrochemical merits offered by dialkylimidazolium ionic liquids.\textsuperscript{2}

Previous electron and mass transport studies in polyether-based molten salts provide ample insights into the dynamics of homogeneous electron self-exchange (or electron hopping) reaction in semi-solids.\textsuperscript{12b,d,17} Recent results have supported a counterion relaxation controlled electron transfer model, that basically says that the electron transport rate is controlled by the electrostatic relaxation of ionic atmosphere around the electron donor-acceptor pair due to the intrinsic ion pair nature of undiluted redox molten salts.\textsuperscript{18} The previous evidence for this kind of electron transport control has come from work on polyether-based molten redox phases. It is thus highly desirable to probe redox semi-solid systems that have similar fluidity and ionic nature, but significantly different molecular structures, such as imidazoliums.

The combination of redox entity (e.g., ferrocene) and imidazoliums can be achieved by covalently linking the redox compound with the alkyl chain of dialkylimidazolium. Thanks to the synthetic work done by Dr. Ramjee Balasubramanian in this laboratory\textsuperscript{20}, a series of ferrocene-attached dialkylimidazolium has been prepared with different linker and side chain structures, as shown in Figure 5.1. While the initial salt products have bromide
counterions, a subsequent metathesis reaction gives ILs with various choices of anions including moisture-stable hexafluorophosphate (PF$_6^-$) and tetrafluoroborate (BF$_4^-$) anions.\textsuperscript{1-2}

The physical properties of these materials, including density, viscosity, and ionic characteristics, are reported in this chapter. The fluidity of ferrocenated imidazolium ionic liquids with varying alkyl chain length shows trends opposite to that of $N,N'$-dialkylimidazoliums, a result we try to understand on the basis of classical free volume theory.\textsuperscript{19} The absorbance spectra of ferrocenated imidazoliums in dilute solution are also discussed; the results, along with mass spectral and NMR data gathered by Dr. Balasubramanian,\textsuperscript{20} are consistent with the formation of chemical linkage between ferrocene and dialkylimidazolium.

### 5.2 Experimental

**Chemical and Reagents.** All chemicals and solvents were used as received.

**Synthesis.** All ferrocenated dialkyimidazoliums were prepared by Dr. Ramjee Balasubramanian as reported in our publication.\textsuperscript{20}

**UV-Vis Spectra.** UV-Vis spectra were obtained from dilute dichloromethane solution of imidazoliums in 1 cm quartz cuvettes on a Shimadzu UV-1601 spectrometer with reference to the blank solvent. Quantitative measurement of absorbance coefficient was based on the spectra of a series of solutions with different concentration. The slope in a linear plot of absorbance vs. molar concentration gave the absorbance coefficient.

**Density.** Room-temperature densities of the imidazoliums were obtained by suctioning the viscous samples (with warming to reduce viscosity if necessary) into a pre-weighed 1 µL capillary (Drummond MicroCaps), using a syringe fitted with an adapter.
Figure 5.1 Basic structure of ferrocenated imidazolium ionic liquids.
LINKER

X = Br, PF$_6$, BF$_4$

SIDECHAIN

SIDECHAIN = CH$_3$,
C$_4$H$_9$, C$_2$H$_4$OCH$_3$

n = 3, 6; m = 4, 6

LINKER = COOCH$_2$C$_n$H$_{2n}$
C$_n$H$_{2n}$, C$_2$H$_4$OC$_2$H$_4$
Viscosity. A cone-plate rheometer (Brookfield digital viscometer, Model DV3, CP52 cone) was used to determine the viscosity of selected ionic liquids at various temperatures which were controlled by a RTE-140 NesLab circulator. At least one hour was required for thermal equilibrium at each temperature prior to measurements. The viscosity at each temperature was measured at several steps by increasing spin rate (shear rate) which was manually programmed on the rheometer. The values of viscosity, shear rate, shear stress and torque could be read out directly from the rheometer after each measurement.

5.3 Results and Discussion

5.3.1 Structure

Three series (labeled #1, 2, and 3) of structurally-different ferrocenated imidazolium ionic liquids were synthesized, as shown in Table 5.1. The first two series of ILs rely on alkyl and alkylester linkages. Ethylene oxide is incorporated in the third series as an early synthetic step to combine poly(ethylene) glycol (however in this case with only one repeat unit) and imidazoliums. The difference between first two series of ILs lies on the linkage between Fc and alkyl chain of imidazoliums. Other structural variations in all three series of ILs include modifications in a) the length of alkyl group between Fc and imidazoliums (C3, C6, C11), b) the side alkyl group on the other side of imidazolium (-Me, -Bu), and c) anions (Br⁻, PF₆⁻, BF₄⁻). A general representation of molecular structure of ferrocenated imidazoliums studied in this chapter is shown in Figure 5.1.

5.3.2 Density and Molar Volume
The densities of ILs at ambient condition, with corresponding molar concentrations and molar volumes, are listed in Table 5.1. All ILs have significantly large molar concentrations of ferrocene (> 2 M) and higher densities than water, while there is an obvious dependence of density on the specific molecular structure of ferrocenated imidazoliums.

As the alkyl chain length on either side of imidazole increases, both molar concentration of ferrocene and density of ILs decrease, for all the anions examined. The trend of density change agrees with that observed by Huddleston et al. and can be explained as a result of addition of lower density -CH₂- groups to the higher density Fe and imidazolium rings. On the basis of this hypothesis, the difference of densities can be transformed into that of molar volumes (\(V_m\)) which can be plotted as a function of number of -CH₂- groups, as illustrated in Figure 5.2. Obviously, the molar volumes of ILs increase (and the density decreases) as the alkyl chain length increases. By assuming an equal volume contribution from each methylene group in the molecular structure, a simple linear correlation can be obtained:

\[
V_m = V_{CH_2} \cdot n + V_0
\]  (1)

where \(V_m\) is the total molar volume of molecular structure, \(V_{CH2}\) the molar volume of methylene group, \(n\) the number of methylene groups in the molecular structure, and \(V_0\) the molar volume occupied by the groups other than -CH₂- and anions in ILs. The slopes of linear correlation in Figure 5.2 give the molar volume of -CH₂- groups which, in most cases, ranges from 16.1~17.1 cm³/mol, a good agreement with reported literature values.

What should be noted here is that the trend of density change for ferrocenated imidazoliums is opposite to that of \(n\)-alkanes, which increase in density as the hydrocarbon chain length increases. Conboy et al. have speculated that the density of ILs should be
Table 5.1 Structure and physical properties of ferrocenated imidazolium ionic liquids.
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<thead>
<tr>
<th>No.</th>
<th>Cation</th>
<th>Anion</th>
<th>MW /g•mol⁻¹</th>
<th>(d) (/g\cdot cm^{-3}) (25°C)</th>
<th>(C^{\alpha}) /M</th>
<th>(V_m^{\text{cm}^3}) /mol⁻¹</th>
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Figure 5.2 Molar volume of ferrocenated imidazolium ionic liquids as a function of number of CH2 groups in the molecule structure for: [Fc-CO2-Cx-Im-S][PF$_6$] (●, S=Me/Bu, and x=3, 6, 9), [Fc-CO2-Cx-Im-S][BF$_4$] (■, S=Me/Bu, and x=3, 6, 9), [Fc-Cx-Im-S][PF$_6$] (▲, S=Me/Bu, and x=4, 6), [Fc-Cx-Im-S][BF$_4$] (▼, S=Me/Bu, and x=4,6), and [Fc-CO2-L-Im-S][PF$_6$] (♦, L=C2OC2, C3, C6, and S=Me, Bu, C2OMe). According to the equation $V_m=V_{CH2}*n+V_0$, the calculated $V_{CH2}$ and $V_0$ values are 16.1 and 266 for [Fc-CO2-Cx-Im-S][PF$_6$], 16.7 and 241 for [Fc-Cx-Im-S][BF$_4$], 17.1 and 237 for [Fc-Cx-Im-S][PF$_6$], 12.4 and 249 for [Fc-Cx-Im-S][BF$_4$], and 17.1 and 271 for [Fc-CO2-L-Im-S][PF$_6$]. (unit: cm$^3$/mol)
$n = \text{number of CH}_2\text{ groups}$

$V_m / \text{cm}^3\text{mol}^{-1}$

$\begin{align*}
\text{Fc-CO}_2, \text{PF}_6, V_{CH_2} &= 16.1 \text{ cm}^3/\text{mol}, V_0 = 266 \text{ cm}^3/\text{mol} \\
\text{Fc-CO}_2, \text{BF}_4, V_{CH_2} &= 16.7 \text{ cm}^3/\text{mol}, V_0 = 241 \text{ cm}^3/\text{mol} \\
\text{Fc-}, \text{PF}_6, V_{CH_2} &= 17.1 \text{ cm}^3/\text{mol}, V_0 = 237 \text{ cm}^3/\text{mol} \\
\text{Fc}, \text{BF}_4, V_{CH_2} &= 12.4 \text{ cm}^3/\text{mol}, V_0 = 249 \text{ cm}^3/\text{mol} \\
\text{Fc-CO}_2, \text{O}, \text{PF}_6, V_{CH_2} &= 17.1 \text{ cm}^3/\text{mol}, V_0 = 271 \text{ cm}^3/\text{mol}
\end{align*}$
more governed by electrostatic interactions than van der Waals forces, which are important in alkanes. The increase of alkyl chain length leads to a larger charge separation and stronger dielectric shielding of charge, therefore reducing the density of ILs. The significance of electrostatic interaction on densities of ILs is more evident from the density data of ILs with different anions. As shown in Table 5.1, all ILs with anions of BF$_4^-$ have larger densities than those with anions of PF$_6^-$, provided the imidazolium structure is otherwise the same. Thus, the corresponding molar volumes of ILs with PF$_6^-$ anions are larger than those with BF$_4^-$ anions. The average molar volume difference between ILs with PF$_6^-$ anions and those with BF$_4^-$ anions is 21.7 cm$^3$/mol. However, the reported van der Waals volume difference between PF$_6^-$ and BF$_4^-$ anions is only 12.0 cm$^3$/mol. Given the strong Coulombic forces in ILs, the discrepancy of volume difference can be attributed to the smaller size of BF$_4^-$ which have larger charge density than PF$_6^-$ and therefore increased electrostatic interaction with imidazolium cations.

The molar volumes can be used to evaluate the volume contribution of the organic groups comprising the ferrocenated imidazolium ionic liquid. For example, in Figure 5.2, the $V_0$ values from structurally different ILs are the summation of volume contributions from all groups other than the methylene groups and anions in the ILs. The difference of $V_0$ between first (●) and second (▲) series of ILs (both with PF$_6$ anions) reflects molar volume of ester group while the molar volume of ether oxygen can be obtained from the $V_0$ difference between the first (●) and third series (◊) of ILs. In this way, the molar volumes of ester group and ether oxygen are calculated as 29 cm$^3$/mol and 5 cm$^3$/mol, respectively, which reasonably agree with the literature value (15.5~23.9 cm$^3$/mol for –COO- and 5.5~6.7
cm$^3$/mol for –O-) obtained from polymers.$^{22b}$ The molar volume of group contributions can be further used for the calculation of fractional free volume of ILs as discussed below.

5.3.3 Fluidity

All of the ferrocenated imidazoliums are amorphous liquid-like phases at room temperature, the only exception being [Fc-C6-Im-Me][PF$_6$] which has a melting point of ca. 102°C. The viscosities of five different ILs were measured as a function of temperature and shear rate. The ILs selected represent four different structural combinations of ester linkage, alkyl chain length, and ethylene oxide group. The viscosity data at room temperature, as shown in Table 5.2, cover a range of four orders of magnitude difference (10$^3$ ~ 10$^7$ cP). The most viscous IL is the one having ester linkage and shortest alkyl chain length. ILs are more fluid when combined with longer alkyl chain or ethylene oxide groups. The least viscous ferrocenated imidazolium among five ILs has a structure free of ester linkage and a moderate length of alkyl chain.

There are several important observations when the viscosity of ferrocenated imidazolium ionic liquid is concerned. First of all, the incorporation of solid-phase ferrocene into ILs induces a significant viscosity increase compared to unferrocenated ILs. The viscosity of dialkylimidazolium ionic liquid without the linked ferrocene depends, not surprisingly, on the specific structure of cations and anions and varies from tens to hundreds of centipoises at room temperature.$^7$ Although more viscous than conventional organic solvent, they are much more fluid than the ferrocenated imidazolium ionic liquids studied here. Secondly, there is an obvious further viscosity increase for the ferrocenated ILs having ester linkages. The rigidity of ester group in the molecular structure may prohibit the free
Table 5.2 Structure and physical properties of ferrocenated imidazolium ionic liquids: viscosity, ionic conductivity and physical diffusion coefficients of ions.
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<th>$E_\sigma$ /kJ·mol$^{-1}$</th>
<th>$D_{\text{RNN}}$ /cm$^2$·s$^{-1}$ (25°C)</th>
<th>$\eta$ /cP (25°C) ($E_{A,\eta}$, kJ/mol)</th>
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rotation/deformation of molecules, resulting in a less fluid sample. Lastly and most interestingly, the viscosity of ferrocenated imidazoliums decreases as the alkyl chain length increases, which is opposite to the trend observed for dialkyimidazolium ILs which show slightly increased viscosities with longer alkyl chains due to the influence of van der Waals interactions.\textsuperscript{23, 7} As discussed above, the inclusion of ferrocene in the molecular structure has a pronounced effect on the viscosity and is probably more significant than the non-polar interaction between alkyl chains since the variation of chain length has only subtle effect on the viscosity, at least in the regime of short chain length.\textsuperscript{23, 24a} While the longer alkyl group would induce larger van der Waals interaction and otherwise larger viscosity, the ferrocene concentrations is also diluted by longer alkyl chain. Given the substantial influences of ferrocene on the fluidity, it is no surprise to see the effect of chain-chain van der Waals interaction, which only subtly affects the viscosity, is over-whelmed by the ferrocene concentration change. The observed viscosity data show that the ferrocenated imidazolium with long alkyl chain has smaller concentration of ferrocene and is more fluid.

As a matter of fact, this trend of viscosity change has been also observed before in hybrid redox polyether molten salts which become less viscous as the polyether chainlength\textsuperscript{12c} or number of chains\textsuperscript{25} is increased, at least in the realm of short chainlength. The results were interpreted on the basis of free volume theory assuming that the free volume content is proportional to the amount of introduced polyether chain.\textsuperscript{17b} According to the free volume theory, the viscosity, an indication of ionic diffusivity, should be exponentially related to the inverse of fractional free volume ($FFV$).\textsuperscript{19} For some ferrocenated imidazolium ionic liquids, a plot of $\ln(\eta)$ vs. $1/FFV$ is obtained as shown in Figure 5.3. Despite the limited
number of viscosity data points, a rather linear correlation is observed, suggesting a possible free-volume-governed fluidity change for ferrocenated imidazolium ionic liquid.

The viscosity measurements of ferrocenated imidazolium ionic liquids are carried out under varied shear rates. As shown in Figure 5.4, all measured ILs show Newtonian behavior with linear correlation between shear stress and shear rate. At a fixed shear rate, no obvious dependence of viscosity on the measuring time is observed. The isotropic Newtonian behavior of ILs has been observed before by Seddon et al. for 1-alkyl-3-methylimidazolium with short alkyl chains (n=2~11). It seems that the incorporation of ferrocene in ILs does not alter the Newtonian fluid nature of ILs.

The viscosity is also measured at different temperatures (25~75°C). As illustrated in Figure 5.5, the viscosity decreases as temperature increases, a trend in an agreement with the observation on dialkylimidazolium ionic liquids. The ferrocenated imidazolium ionic liquids show Arrhenius-type behavior in the temperature range studied, as given by the equation,

$$\eta^{-1} = Ae^{-\frac{E_A}{RT}}$$  \hspace{1cm} (2)

where $\eta$ is the viscosity and $E_A$ is the activation barrier for viscous flow. Some deviation from the linear correlation is observed at lower temperature and could be due to the onset of ion association and aggregation at the temperature near melting point as claimed by Cratzel et al. However, our transport study in some metal complex polyether molten salts also yields similar curvature in Arrhenius plot despite the fact that the temperature range explored is far beyond the melting point or glass transition temperature of material. The resulting curvature is believed to be due to the strong coupling of polyether chain motion with the transport process. Similar coupling of alkyl segmental chain motion with the
Figure 5.3 Relationship between viscosity (25°C) ($\eta$) and the fractional free volume ($FFV$) for ferrocenated imidazolium ionic liquid, [Fe-CO2-Cx-Im-Bu][PF6]. x=3, 6, 11.
$\ln(\eta/\eta P)$ vs $1/FFV$

$[\text{Fc-CO}_2-\text{C}_x-\text{Im-Bu}][\text{PF}_6]$, $X=3, 6, 11$
Figure 5.4 Viscosity measurement at different shear rate. The linear correlation between shear stress and shear rate indicates that viscosity is independent on the shear rate, a typical Newtonian fluid behavior.
Figure 5.5 Viscosities of selected ionic liquids at different temperatures
forced ionic transport in viscosity measurements could also happen in present case of ferrocenated imidazoliums and give curved Arrhenius plots.

For the convenience of comparison, the viscosity thermal barriers are calculated by forcing a linear fitting over different regions of the entire temperature range; the results are listed in Table 5.2. The barriers of viscous flow obtained from ferrocenated imidazoliums are much larger than those of dialkylimidazoliums, of which, the reported barriers range from 21 kJ/mol\(^{23}\) to 38 kJ/mol\(^{26}\), depending on the specific cation and anion structure. For ferrocenated imidazoliunm themselves, there is also an obvious dependence of the energy barrier on the structure. For example, a larger barrier, along with the larger viscosity, is observed with ferrocenated imidazoliums with shorter alkyl chains. The large viscosity of ferrocenated imidazolium should be accounted, at least partially, by the large barriers to viscous flow.

5.3.4 Ionic Characteristics

Ionic conductivities of the new ferrocenated imidazolium ILs were measured at various temperatures from 25°C to 75°C. The values of both conductivity and its thermal barrier (from Arrhenius plot) are listed in Table 5.2. The physical diffusion coefficients of ions are calculated according to Nernst-Einstein equation:\(^{12b,27}\)

\[
\sigma_{ION} = \frac{F^2}{RT} \left[ z^2_{Im}, D_{Im}, C_{Im}^{-} + z^2_{CION}, D_{CION}, C_{CION}^{-} \right] = \frac{F^2 Z C}{RT} \left[ D_{Im}^{-} + D_{CION}^{-} \right] \quad (3)
\]

where \(z, D, \) and \(C\) are charge, diffusion coefficient, and concentration of the indicated species, respectively. Clearly, the calculated ionic diffusion coefficient \((D_{ION})\) is actually the summation of physical diffusion coefficients of both cation \((D_{IM}^{-})\) and anions \((D_{CION})\). However, given the size difference between ferrocenated imidazolium cations and anions...
Figure 5.6 Relationship between diffusion coefficients of ions and viscosity for selected ferrocenated imidazolium ionic liquids at 25°C. The data of diffusion coefficients, viscosity and structure of ionic liquids are listed in Table 5.2.
(PF₆ or BF₄), it seems reasonable that ionic conductivity of ferrocenated imidazolium ionic liquid will be dominated by the smaller anions, which should be much more mobile than the bulky redox imidazolium cations.¹²b,c

The ionic conductivities of ionic liquids and the diffusion coefficients of their constituent ions can be related to fluidity. As shown in Figure 5.6, the physical diffusion of PF₆ anions qualitatively follows inverse of viscosity in various ILs as predicted by a modified Einstein-Stokes equation correlating the ionic transport to viscosity of medium even in molten salts:²⁸

\[
D = \frac{kT}{6\pi r \xi \eta}
\]

where \( r \) is the hydrodynamic radius of diffusive species, \( \xi \) the microviscosity factor of ions, \( \eta \) the viscosity, \( k \) Boltzmann constant and \( T \) the temperature. A quantitative linear behavior is, however, not found in Figure 5.6, nor is it necessarily expected. There is no direct evidence that \( r \) and \( \xi \) should be constant in different ionic liquids where the ions are so concentrated that the solvation of ions is far from complete and may depend on the specific structures.²³

As a matter of fact, even for the same ionic liquid, \( r \) and \( \xi \) may also depend on the viscosity and yield non-linear \( D - \eta^{-1} \) deviation from equation (4). The obvious evidence is that the temperature-dependence measurements of \( D \) and \( \eta \) show dramatically different dynamics. As listed in Table 5.2, the thermal barriers of ionic conductivity, when compared with those of viscosity, are much smaller. It should be noted that the conductivity of ferrocenated imidazolium ionic liquids is dominated by the mobility of smaller anions while the bulky redox cations essentially remain on the equilibrium position without significant relative motion.¹²b,c, ⁸a The barriers of conductivity, therefore, reflect the dynamics of anions. The viscosity measurements involve instead, significant, enforced relative motions of both
cation and anions. It certainly requires more energy for the large ferrocenated imidazolium cation to move through the neighboring cationic structure than for the relatively smaller anions in highly concentrated ionic liquid. Therefore, a larger thermal barrier from viscosity measurement is likely due to the energy contribution from the dynamics of imidazolium cation motions. As indirect evidence, the Arrhenius plots (not shown) of ionic conductivity are linear, in contrast with the curvature in viscosity measurements. The linear Arrhenius behavior of ionic conductivity suggests that the ionic transport process involves no strong coupling to the alkyl chain segmental motions. In another word, the contribution of physical diffusion of imidazolium ions in ionic transport is insignificant.\textsuperscript{12c,27,29}

As discussed above, it is observed that the ferrocenated imidazoliums become less viscous as the alkyl chain length increases, at least in the realm of short chain lengths. This characteristic implies that the ionic liquid physical properties, $D_{\text{ION}}$ and $\eta$, might be quantified in terms of the volume fraction of alkyl groups present.\textsuperscript{17b} We assume here that the free volume content of the ILs is proportional to the number of CH$_2$ groups, each of which occupies a volume determined from Figure 5.2. According to the free volume theory, the diffusivity should be exponentially related to the inverse of free fractional volume ($1/FFV$).\textsuperscript{1}

Figure 5.7 shows plots of ln($D_{\text{ION}}$) versus $1/FFV$ for the various ferrocenated imidazolium ionic liquids. $FFV$ was calculated according to:\textsuperscript{17b,19}

$$FFV = \frac{V_{\text{CH}_2} \cdot n_{\text{CH}_2}}{V_m}$$

where $V_{\text{CH}_2}$ is the molar volume of methylene group, $n$ the number of methylene groups (including side groups) and $V_m$ the molar volume of ionic liquid. The linear correlations between ln($D_{\text{ION}}$) and $1/FFV$ are generally observed for ILs with different side groups and
anions. Despite the limited number of data points and some deviations, the trend of increasing ionic mobility with the volume fraction seems to be present and shows a concept of “equal-methylene-content”, at least for the ferrocenated imidazolium ionic liquids with short alkyl chains.

5.3.5 Absorbance Spectra

Selected UV-Vis spectra of three ferrocenated imidazolium ionic liquids in dilute methylene chloride solutions along with the spectra of ferrocene and ferrocenium are shown in Figure 5.8. The absorbance feature of ferrocenated imidazoliums is quite similar to that of Fc with characteristic peaks at ca. 440 nm and 320 nm. There is no strong absorbance contribution from the imidazoliums themselves (see the inset of Figure 5.8) except at much shorter wavelengths. For some early batches of ILs, another band appeared at around 620 nm which is symptomatic of partial oxidation of ferrocene to ferrocenium during the synthesis or workup. An improved synthetic and purification route solved this problem and all samples studied are free of the oxidized form.

Quantitative measurement of absorbance coefficients at ca. 440 nm of ferrocenated imidazoliums was conducted in dilute methylene chloride solutions with varying IL molar concentrations. As obvious from Table 5.3, the absorbance coefficients of ILs with ester linkage between Fc and alkyl chain are much larger than those without ester groups. The same trend is also observed when absorbance coefficients of monomer n-alkylferrocene and ferrocenecarboxylic acid are compared. Clearly, the UV-Vis spectra provide extra evidence to the covalently-attachment of ferrocene to imidazolium ionic liquids.
Figure 5.7 Relationship between physical diffusion coefficients (75°C) of ions ($D_{ION}$) and the fractional free volume ($FFV$) for a variety of ferrocenated imidazolium ionic liquids: (A) [Fc-CO2-Cx-Im-Me][PF$_6$] (●), [Fc-CO2-Cx-Im-Me][BF$_4$] (■), [Fc-CO2-Cx-Im-Bu][PF$_6$] (▲), and [Fc-CO2-Cx-Im-Bu][BF$_4$] (▼). x=3, 6, 11; (B) [Fc-Cx-Im-S][Y] (●, x=4,6, S=Me/Bu, and Y=PF$_6$/BF$_4$ excluding one datum point shown as ■).
(B) $x=6, S=\text{Bu}, Y=\text{PF}_6$

$x=4, S=\text{Bu}, Y=\text{PF}_6$

$x=4, S=\text{Bu}, Y=\text{BF}_4$

$x=6, S=\text{Bu}, Y=\text{BF}_4$

$x=4, S=\text{Me}, Y=\text{PF}_6$

$x=4, S=\text{Me}, Y=\text{BF}_4$
**Figure 5.8** UV-Vis spectra of selected ferrocenated imidazoliums in dilute methylene chloride solutions. As comparison, the UV-Vis spectra of ferrocence, ferrocenium hexafluorophosphate and 1-hexyl-3-methylimidazolium hexafluorophosphate are shown in the inset.
Wavelength /nm
400 600 800 1000

Absorbance Coefficient /M$^{-1}$cm$^{-1}$
0

[Fc-CO$_2$-C$_6$-Im-Bu]
[Fc-C$_6$-Im-Bu]

Absorbance (a.u.)
0.0

Wavelength /nm

Absorbance Coefficient /M$^{-1}$cm$^{-1}$
2500
2000
1500
1000
500
0

sign of Fc oxidation

198
Table 5.3 UV-Vis absorbance coefficients of selected ferrocenated imidazoliums as compared to ferrocene and its derivatives in dilute methylene chloride solutions at one of the absorbance maxima ($\lambda_{\text{max}}$).
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<th>[Fc-CO2-C3-Im-Bu]</th>
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<td>$\varepsilon$/M$^{-1}$cm$^{-1}$</td>
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<td>$\varepsilon$/M$^{-1}$cm$^{-1}$</td>
<td>83</td>
<td>97</td>
<td>96</td>
<td>283</td>
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Hendrickson, S. M.; Malik, M. A.; Miecznikowski, K.; Murray, R. W.  

Murray, R. W.  


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24. (a) Holbrey, J. D.; Seddon, K. R. J. Chem. Soc., Dalton Trans. 1999, 13, 2133. (b) Some non-Newtonian fluids show a time-dependent change in viscosity. If the apparent viscosity increases with duration of stress, the fluid is called rheopectic. The opposite type of behavior, in which the fluids become less viscous the longer they under shear, is called thixotropy.


6.1 Introduction

It has shown in a number of studies that $N,N'$-dialkylimidazolium ionic liquids (ILs) can be used as solvents for redox species and for electrochemical reactions. Helpful are physical and chemical properties like intrinsic ionic conductivity, low vapor pressure, chemical stability, and solubility of a wide range of organic and inorganic compounds.\(^1\) The typical electrochemical study in ionic liquids as solvents is carried out in a bulk volume with small concentration of dissolved redox species. Alternatively, the ILs can be used as electrolytes covering a solid layer of redox compounds adhered to the electrode surface.\(^2\) In this chapter, we present some electrochemical results based on imidazolium ionic liquids in which redox compounds, e.g., ferrocene, are covalently linked with imidazolium cations. The resulting intrinsically electroactive ionic liquid has a high concentration of redox sites (> 2 M, see Chapter V), which favors electron hopping reactions for charge transport, in comparison to the physical diffusion of redox ions which is depressed due to the viscosity increase with the inclusion of ferrocene. That is, homogeneous electron transfer reactions become a
relatively efficient way of charge transport in this unique environment of redox-attached imidazolium ionic liquids. Other reports of electron hopping effects in imidazolium-based ionic liquids are quite limited, and most examples involve the iodide/triiodide redox couple in ionic liquids for solar energy conversion application.\textsuperscript{3,4}

There is a long-term interest in our laboratory to explore electron and mass transport dynamics in redox semi-solids or molecular molten salts.\textsuperscript{5-9} As a general route, the redox melt has been formed by chemically attaching low molecular weight poly(ethylene) glycol (PEG) to the redox compound \textsuperscript{5-7} or to its counterion \textsuperscript{8-9}. The resulting material is highly viscous, amorphous at room temperature and possesses a high concentration of redox sites so that charge transport by electron hopping reaction is favored. These materials have been called redox polyethers or redox polyether hybrids.

The electron transfer dynamics studies in the redox polyethers have been focused on the fundamental understanding of the effect of local structural/environmental factors on the electron transfer reaction and ensuing charge transport.\textsuperscript{6b,d,10} While our earliest analysis of the process proposed a solvent dynamics control, recent results from various metal complex polyether melts\textsuperscript{11} and Au nanoparticle molten salt\textsuperscript{12} have led us to an improved and we believe more correct theoretical transport model, namely, ionic atmosphere relaxation controlled electron transfer.\textsuperscript{11-12} In this model, the measured electron transport rate is dependent on the diffusive relaxation of counterions around the electron acceptor-donor pair, and does not reflect the intrinsic dynamics of the electron transfer reaction. All of our previous studies of this model have been based on the hybrid redox polyethers. Here, we study the electron transport dynamics in a completely different chemical system, in which a
redox probe is combined with imidazolium cations. This provides an opportunity to explore this fundamental matter in a chemically more general way.

Chapter V focused on the discussion of structures and physical properties of ferrocenated imidazoliums. This chapter will mainly deal with electrochemical aspects of ferrocenated imidazoliums and especially the electron transport dynamics in such media. In this chapter, the cyclic voltammetry of various ferrocenated imidazolium ionic liquids in either dilute solution or undiluted state is examined. The electron and ionic mass transport are quantitatively measured with the IL phase contacted by either vacuum or high pressure CO₂. A linear correlation with unity slopes between electron transport rate constant ($D_{\text{APP}}$) and ionic diffusion ($D_{\text{ION}}$) is observed for various structurally-different ferrocenated imidazoliums. The result agrees excellently with the context of ionic atmosphere relaxation controlled electron transfer model, explored previously in the polyether melts\textsuperscript{11-12} but here for the first time in imidazolium-attached ionic liquids.

6.2 Experimental

**Voltammetry in Dilute Solutions.** Cyclic voltammetry was performed in solutions of dichloromethane/0.2 M Bu₄NClO₄ (Fluka) in cell vials (BAS) using Pt disk (1.6mm dia.) working, Pt coil counter and aqueous Ag/AgCl/0.1M NaCl reference electrodes using a CH Instruments Electrochemical Workstation.

**Electrochemistry in Undiluted Ionic Liquids.** The electrochemical measurements in undiluted ILs are done as previously described for redox polyether hybrids.\textsuperscript{11-12} Basically, \textit{ca.} 10 mg of ILs are drop-cast onto the platform of home-made four-electrode assembly which consists of a 25 µm dia. Pt micro-disk working electrode, a Ag quasi-reference electrode and
two 0.4 mm dia. Pt disk electrodes (for ionic conductivity measurements, one of them can work as the counter electrode in 3-electrode voltammetry). The electrode assembly is placed in \( \frac{1}{4} \) in. stainless steel tube with both ends sealed with epoxy resin and proves to be durable in both vacuum and high pressure environment for electrochemical measurements. Samples are dried at elevated temperature (75\(^\circ\)C) in vacuum for at least 12 hours prior to the measurements. The electrochemistry is performed in active vacuum, and the droplet of ILs on the electrode and the whole cell enclosure are pre-equilibrated at each temperature for at least 2 hours. Both voltammetry and AC impedance (for ionic conductivity measurements) are carried out in a Faraday cage with a CH Instruments Electrochemical Station.

AC impedance measurement of ionic conductivities was conducted over a frequency range of 0.1 Hz to 100 kHz, at 0 V dc bias and 50 mV amplitude, on two 0.4 mm dia. Pt disk electrodes. Ionic conductivity was calculated as the ratio of geometric cell constant (calibrated by standard solutions) and cell resistance taken from the low frequency real-axis intercept of the complex impedance semicircle in Nyquist plot.

**Digital Simulations.** Digital simulations of cyclic voltammograms (10 mV/s) in undiluted [Fc-CO2-C6-Im-C2OMe][PF\(_6\)] at 75\(^\circ\)C are carried out with DigiElch2 (http://www.digielch.de, copyright by M. Rudolph) with and without consideration of \( iR_{UNC} \) effect. The values of input parameters are \( R_{UNC}=1.43\times10^7 \ \Omega \), \( r = 12.5 \ \mu\text{m} \) (disk electrode radius), ferrocene site concentration \( C=2.31 \ \text{M} \), \( \alpha=0.5 \), and \( k_s=10^5 \) to \( 10^{-5} \) cm/s. \( D \) is varied to match peak current amplitudes of simulated and experimental CVs. The results show that the experimental peak separation is dominated by \( iR_{UNC} \) distortion. Varying the \( k_s \) value has far less effect on \( \Delta E_{p} \), even down to unrealistically small values for ferrocene.
**High-Pressure CO\(_2\) Experiment.** A home-made stainless steel high-pressure cylindrical cell with two sapphire windows is used for CO\(_2\) experiment at high pressure. The CO\(_2\) gas is introduced into the cell using a syringe pump (Model 260 D, Isco) with the pressure monitored by an output pressure transducer (Model TJE AP121DV, Sensotec). The temperature of the CO\(_2\) cell is controlled by using a water jacket connected to a Neslab RTE-110 circulator. The real temperature is monitored by a thermocouple inserted into the CO\(_2\) chamber. The high-pressure electrode assembly is inserted into the CO\(_2\) cell with the ILs on the top of the electrode. The samples are equilibrated at each CO\(_2\) pressure and temperature for at least 2 hours prior to the measurements.

### 6.3 Results and Discussion

#### 6.3.1 Voltammetry in Dilute Solutions

Cyclic voltammograms of ferrocenated imidazoliums in dilute methylene chloride solution are shown in Figure 6.1, along with the voltammogram of ferrocene itself. The dilute solution CVs are unremarkable, basically showing single well-defined Fc\(^{+1/0}\) redox waves similar to that of ferrocene. The formal potentials of ferrocenated imidazoliums are characteristic of linkage between ferrocene and dialkylimidazolium. For those with electron-withdrawing ester group, the formal potential is *ca.* 0.2 V more positive of ferrocene while alkylated ferrocene imidazoliums are *ca.* 50 mV more negative due to the slight electron-donor effect of alkyl group to ferrocene. The result from the electrochemistry agrees with the UV-Vis absorbance spectra\(^{13}\), confirming the formation of ferrocenated imidazoliums.

The attachment of the imidazolium structure does not obviously alter the reversibility of ferrocene. As illustrated in Figure 6.2 where the peak potential separation (\(\Delta E_p\)) is...
Figure 6.1 Cyclic voltammograms (50 mV/s) of ferrocenated imidazoliums in dilute methylene chloride solutions containing 0.2 M Bu$_4$NClO$_4$ as supporting electrolyte. The molar concentrations are 1.6 mM, 1.2 mM, and 0.9 mM for [Fc-CO$_2$C$_6$-Im-Me], [Fc-CO$_2$C$_2$OC$_2$-Im-Me], and [Fc-C$_6$-Im-Me], respectively. The cyclic voltammogram of ferrocene is also included for the purpose of comparison.
**Figure 6.2** Peak potential separation ($\Delta E_p$) as a function of peak current ($i_p$) for cyclic voltammogram of [Fe-CO2-C6-Im-Me] at different scan rate. The intercept of linear correlation is 55 mV.
\[ \Delta E_p = \Delta E_p^0 + 2i_P R_{\text{UNC}} \]

- \( \Delta E_p = 55 \text{ mV} \)
- \( i_p \) values: 0, 5e-6, 1e-5, 2e-5, 3e-5, 3e-5
- Voltage rises as \( i_p \) increases.
- Linear relationship shown on the graph.

Graph dimensions: 612.0x792.0
**Figure 6.3** Microelectrode cyclic voltammogram of undiluted ferrocenated imidazolium, [Fc-CO2-C6-Im-C2OMe][PF₆], at (a) varied temperatures (10 mV/s) and (b) different scan rates (75°C) on 12.5 µm Pt disk electrode in vacuum.
extrapolated as a function of peak current ($i_p$) back to zero scan rate, the linear extrapolation gives an intercept of 55 mV. This is the peak-potential spacing without the complication of $iR_{UNC}$ effect, and close to the thermodynamic value for an ideal reversible reaction (58 mV at 20°C).\textsuperscript{14}

### 6.3.2 Voltammetry in Undiluted Ionic Liquids

Phenomenologically similar to the voltammetry obtained in the dilute solution, the electrochemistry in undiluted, neat ferrocenated imidazolium ionic liquids yields again a single well-defined Fe$^{+1/0}$ wave, as shown in Figure 6.3. However, due to the lack of solvent, the undiluted ionic liquids have only moderate ionic conductivity\textsuperscript{13} which results a significant uncompensated resistance as demonstrated by the much larger peak potential separations than in dilute solutions in spite of use of a micro-disk electrode (12.5 µm radius) and slow scan rate (10 mV/s). A calculation of the $iR_{UNC}$ effect, assuming the measured ionic conductivity of 4.63x10$^{-6}$ Scm$^{-1}$ for the ferrocenated ionic liquid shown in Figure 6.3 at 75°C, gives 1.43x10$^7$ Ω of uncompensated resistance ($R_{UNC}$)$^{14,15}$, which corresponds to ca. 424 mV of $iR_{UNC}$ potential separation\textsuperscript{16}. The actual peak spacing between anodic and cathodic scan ($\Delta E_p$) in Figure 6.3 is 498 mV, which, after a simple subtraction of $iR_{UNC}$ effect, should be corrected to 74 mV. As a comparison, the thermodynamic potential peak spacing for a reversible one electron electrochemical reaction is 69 mV at 75°C.\textsuperscript{14} The reversibility of Fe$^{+1/0}$ is further confirmed by voltammetric digital simulation. As shown in Figure 6.4, with assumed reversibility ($k_s$=10$^5$ cm/s) and including only the $iR_{UNC}$ effect, the simulated voltammogram agrees quite well with the experimental results.
The $iR_{\text{UNC}}$ effect is also evident in the temperature and scan rate dependence experiments (see Figure 6.3). At a given temperature, slower potential scan rates give smaller peak potential separations. The smaller current resulting from the slower scan rate gives a smaller $iR$ drop. At constant scan rate, the peak potential spacing is also smaller at higher temperature due to the reduced $iR_{\text{UNC}}$ effect ($i \propto D^{1/2}$, $R \propto D^{-1}$).\(^{14}\)

A few more examples of cyclic voltammograms from various ferrocenated imidazolium ionic liquids are illustrated in Figure 6.5. Each of them represents a typical structure from three series of ionic liquids as discussed in Chapter V. Again, the cyclic voltammograms are characteristic of the Fc$^{+1/0}$ reaction with imposed distortion due to the $iR_{\text{UNC}}$ effect.

### 6.3.3 Electron Transport Measurements

The electrochemistry in undiluted ferrocenated imidazolium ionic liquids is different from that in dilute solutions in that the concentration of redox entities ($>2$ M for ferrocenated imidazoliums)\(^{13}\) is very high. Thus, the electron self-exchange (electron hopping) reaction can readily happen between different redox sites. The current collected by the electrode is in principle governed by both physical diffusion of redox species and the electron diffusion as a result of electron self-exchange reactions. The overall, apparent diffusion coefficient ($D_{\text{APP}}$), according to the theories of Dahms-Ruff, can be expressed as:\(^{17}\)

$$D_{\text{APP}} = D_{\text{PHYS}} + D_{E} = D_{\text{PHYS}} + \frac{k_{\text{EX}} \delta^{2} C}{6}$$  \(1\)

where $\delta$ is the average equilibrium center-to-center distance between neighboring redox sites and $C$ is the total concentration of redox sites. Given the high viscosity of ferrocenated imidazoliums and bulky size of imidazolium cations compared to the smaller anions (PF$_6$, \(216\))
**Figure 6.4** Digital simulation of cyclic voltammogram (10 mV/s) in undiluted [Fe-CO2-C6-Im-C2OMe][PF6] at 75°C with and without consideration of $iR_{\text{UNC}}$ effect. ($R_{\text{UNC}}=1.43\times10^7 \Omega$)
Potential /V

0.0 0.2 0.4 0.6 0.8 1.0

Experimental: $k_s=10^5$ cm/s, $R_{UNC}=0$ Ω

Simulated:
- $k_s=10^5$ cm/s, $R_{UNC}=1.4 \times 10^7$ Ω
- $k_s=10^{-5}$ cm/s, $R_{UNC}=0$ Ω

10 nA

Potential /V
Figure 6.5 Microelectrode cyclic voltammogram (10 mV/s) of undiluted ferrocenated imidazolium ionic liquids: [Fc-CO2-C6-Im-Bu] (blue), [Fc-C6-Im-Bu] (red), and [Fc-CO2-C2OC2-Im-Bu] (green) at 75°C on 12.5 µm Pt disk electrode in vacuum.
75°C, 10 mV/s, vacuum

Potential vs. AgQRE (V)

Current (A)

[Fc-CO2-C6][PF6]

[Fc-C6-Im][PF6]

[Fc-CO2-C2OC2-Im-Bu][PF6]
BF₄), the physical diffusion is much less efficient than the electron diffusion and can usually be neglected without significant error.⁶ᵇ,ᶜ,¹¹ᵣ

The measurement of apparent electron transport \((D_{\text{APP}})\) in ferrocenated imidazolium ionic liquids was made with chronoamperometry.¹¹ A potential step from a non-Faradaic region to a diffusion-limited potential of the redox wave is applied for 300-500 s. The recorded current-time response is fit to Cottrell equation to get the diffusion coefficients as illustrated in Figure 6.6.¹⁴,¹⁸ The apparent electron diffusion coefficients obtained from various ferrocenated imidazoliums, along with the data of physical diffusion coefficient of anions obtained from ionic conductivity measurements (see Chapter V), are listed in Table 6.1 and 6.2. The corresponding thermal barriers are obtained from Arrhenius plots of temperature-dependent transport data, as shown in Figure 6.7.

The data in Table 6.1 and 6.2 show that the physical diffusion coefficients of anions are one or two orders of magnitude smaller than those of apparent electron diffusion coefficients. Given the size difference between ferrocenated imidazolium cations and anions of PF₆⁻ or BF₄⁺, one should expect that the physical diffusion of ferrocenated imidazolium cations would be smaller than those of anions. Therefore, the difference between physical diffusion of ferrocenated imidazoliums and electron diffusion should be even larger. With that said, it seems reasonable that the measured apparent diffusion coefficients are predominantly due to the electron diffusion, from which the rate constant of electron transfer reaction between neighboring ferrocene sites can be calculated with equation (1).

It should be noted that there is possible contribution of electronic migration to the measured electron diffusion coefficient since the counterion diffusion coefficients \((D_{\text{ION}})\) are small compared to the electron diffusion coefficients \((D_{E}, \text{or} D_{\text{APP}})\). According to Saveant’s
Figure 6.6. Chronoamperometry of undiluted ferrocenated imidazolium ionic liquids: [Fc-CO2-C6-Im-Bu] (blue), [Fc-C6-Im-Bu] (red), and [Fc-CO2-C2OC2-Im-Bu] (green) at 75°C on 12.5 µm Pt disk electrode in vacuum. The experimental current-time response is fitted into Cottrell equation as shown in black lines.
Table 6.1 Physical transport and electron-transfer results for [Fc-CO2-C6-Im-Bu], [Fc-C6-Im-Bu], and [Fc-CO2-C2OC2-Im-Bu] ionic liquids with PF$_6^-$ anions.
<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>[Fc-CO2-C6-Im-Bu]</th>
<th>[Fc-C6-Im-Bu]</th>
<th>[Fc-CO2-C2OC2-Im-Bu]</th>
</tr>
</thead>
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<tr>
<td><strong>C / M</strong></td>
<td>2.39</td>
<td>2.46</td>
<td>2.51</td>
</tr>
<tr>
<td><strong>η (25°C) / cP</strong></td>
<td>5.81x10^5</td>
<td>8.47x10^3</td>
<td>5.36x10^5</td>
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<td><strong>D_{ION} (25°C) / cm²s⁻¹</strong></td>
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<td>1.68x10⁻¹⁰</td>
<td>9.89x10⁻¹²</td>
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<tr>
<td><strong>E_{A, ION} / kJ mol⁻¹</strong></td>
<td>73</td>
<td>55</td>
<td>81</td>
</tr>
<tr>
<td><strong>D_{APP} (25°C) / cm²s⁻¹</strong></td>
<td>7.48x10⁻¹¹</td>
<td>1.01x10⁻⁸</td>
<td>3.64x10⁻¹⁰</td>
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<tr>
<td><strong>k_{EX} (25°C) / M⁻¹ s⁻¹</strong></td>
<td>2.39x10⁴</td>
<td>3.19x10⁶</td>
<td>1.15x10⁵</td>
</tr>
<tr>
<td><strong>E_{A, ET} / kJ mol⁻¹</strong></td>
<td>76</td>
<td>56</td>
<td>75</td>
</tr>
<tr>
<td><strong>D_{APP, CORR} (25°C) / cm²s⁻¹</strong></td>
<td>4.17x10⁻¹¹</td>
<td>1.17x10⁻⁹</td>
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<td><strong>k_{EX, CORR} (25°C) / M⁻¹ s⁻¹</strong></td>
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<td>3.72x10⁵</td>
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<tr>
<td><strong>E_{A, ET, CORR} / kJ mol⁻¹</strong></td>
<td>76</td>
<td>59</td>
<td>81</td>
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Table 6.2 Physical transport and electron-transfer results for various ferricenated imidazolium ionic liquids in vacuum.
<table>
<thead>
<tr>
<th>No.</th>
<th>Cation</th>
<th>Anion</th>
<th>$D_{ION}$ /cm$^2$/s$^{-1}$ (75°C)</th>
<th>$E_{A,ION}$ /kJ•mol$^{-1}$</th>
<th>$D_{APP}$ /cm$^2$/s$^{-1}$ (75°C)</th>
<th>$E_{A,APP}$ /kJ•mol$^{-1}$</th>
<th>$k_{EX}$ /M$^{1}$•s$^{-1}$ (75°C)</th>
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<td>1</td>
<td>[Fc-CO2-C3-Im-Me]</td>
<td>[PF$_6$]</td>
<td>5.15x10$^{-11}$</td>
<td>107</td>
<td>iR*</td>
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<td></td>
<td></td>
<td>[BF$_4$]</td>
<td>2.44x10$^{-11}$</td>
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<td>iR</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[PF$_6$]</td>
<td>1.90x10$^{-10}$</td>
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<td>----</td>
<td>----</td>
</tr>
<tr>
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<td>[Fc-CO2-C6-Im-Me]</td>
<td>[BF$_4$]</td>
<td>4.65x10$^{-11}$</td>
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<td>iR</td>
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<td>----</td>
</tr>
<tr>
<td>2</td>
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<td>[PF$_6$]</td>
<td>1.99x10$^{-9}$</td>
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<td>1.48x10$^{-8}$</td>
<td>67</td>
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<td></td>
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<td></td>
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<td>iR</td>
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<td>----</td>
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<td>n/a</td>
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<tr>
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<td></td>
<td>[BF$_4$]</td>
<td>2.33x10$^{-9}$</td>
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<td>1.08x10$^{-7}$</td>
<td>56</td>
<td>3.2x10$^7$</td>
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<tr>
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<td>n/a</td>
</tr>
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<td></td>
<td></td>
<td>[BF$_4$]</td>
<td>3.59x10$^{-9}$</td>
<td>68</td>
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<td>58</td>
<td>1.1x10$^8$</td>
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<td></td>
<td>[Fc-C6-Im-Bu]</td>
<td>[PF$_6$]</td>
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<td>2.48x10$^{-7}$</td>
<td>56</td>
<td>7.9x10$^7$</td>
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<td>[BF$_4$]</td>
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<td>n/a</td>
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<td>n/a</td>
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<td>9.70x10$^{-10}$</td>
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<td>81</td>
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<td>[Fc-CO2-C3-Im-C2OMe]</td>
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<td>113</td>
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<tr>
<td></td>
<td>[Fc-CO2-C6-Im-C2OMe]</td>
<td>[PF$_6$]</td>
<td>6.22x10$^{-10}$</td>
<td>79</td>
<td>1.74x10$^{-8}$</td>
<td>73</td>
<td>5.6x10$^6$</td>
</tr>
</tbody>
</table>

* Chronoamperometric measurements not available due to the severe $iR_{UNC}$ distortion
Figure 6.7 Arrhenius plots of apparent electron diffusion coefficients (above) and physical diffusion coefficients of counterions (below) at varied temperatures for selected ferrocenated imidazolium ionic liquids: [Fc-CO2-C6-Im-Bu] (●), [Fc-C6-Im-Bu] (■), and [Fc-CO2-C2OC2-Im-Bu] (▲). The thermal barriers of apparent and ionic diffusion are 76, 56, 75 kJ/mol and 73, 55, 81 kJ/mol, respectively.
\[ \ln(D_{\text{APP, CORR}}/\text{cm}^2\text{s}^{-1}) \]

\[ \ln(D_{\text{ION}}/\text{cm}^2\text{s}^{-1}) \]
theory, the electroneutrality coupling of electron hopping between localized redox sites and electroinactive counterion displacement induces a “migration” enhancement of the potential-step plateau current responses.\textsuperscript{19} The sluggish counterion mobility results in an extra electric field gradient in the sample (also reflected by the $iR_{\text{UNC}}$ effects in the CV results) which effectively enhances the electron hopping reaction and gives an overestimated $D_E$ value. The electronic migration effect can be significant when the ratio of $D_{\text{ION}}/D_E$ is much smaller than one, as in the present case. Therefore, the appropriate correction from the theory of Saveant\textsuperscript{19} was applied. The corrected $D_E$ and $k_{\text{EX}}$ values are listed in Table 6.1 and are \textit{ca.} 2- to 10-fold smaller than the experimental data. The correction was applied to data at all temperatures but has only a minor effect on the thermal barrier values.

The electron transfer rate constants in ferrocenated imidazoliums are in the range of $10^4$ to $10^5$ M$^{-1}$s$^{-1}$. However, the comparable Fe$^{+1/0}$ reaction in dilute acetonitrile solution is much faster, with a rate constant near $10^7$ M$^{-1}$s$^{-1}$.\textsuperscript{20} The smaller electron transfer rate constants in ferrocenated imidazoliums are similar to those observed in dry poly(vinylferrocene) films (in N$_2$ atmosphere), where the $k_{\text{EX}}$ ranges from 5.8x10$^4$ to 4.3x10$^5$ M$^{-1}$s$^{-1}$.\textsuperscript{21} The smaller electron transfer rate constants in ferrocenate imidazoliums are also accompanied by relatively large activation thermal barriers. One significant observation of the data in Table 6.1 is that the electron transfer thermal barrier energies are similar to those of counterion physical diffusion, for various ferrocenated imidazolium ionic liquids with different cationic structure. The similarities in thermal barrier suggest a strong correlation of electron transport dynamics with the ionic transport. Analogous results have been previously analyzed in redox polyether melts on the basis of the ionic atmosphere relaxation model.\textsuperscript{11-12}
6.3.4 Ion Atmosphere Relaxation Controlled Electron Transport

The electron transport studies in various redox semi-solids, from metal complex polyether melts\textsuperscript{11} to Au nanoparticle molten salts\textsuperscript{12}, have established an ion atmosphere relaxation control model for electron transfer, in which the effective electron transport rate (detectable by electrode reaction) is controlled by the diffusive relaxation of counterions around the electron-acceptor pair. The essential idea of this model, where the ion paring effect on electron transfer is considered, can be written in the context of Fc\textsuperscript{+1/0} reaction in ferrocenated imidazoliums as two step processes:\textsuperscript{22}

$$X^{-}Fe^{+1}Fe^{0} \rightleftharpoons k_{1} \frac{k}{k_{-1}} X^{-}Fe^{0}Fe^{+1} \rightarrow Fe^{0}Fe^{+1}X^{-}$$

where the forward electron transfer reaction ($k_{1}$) is followed by the relaxation of counterions ($k_{2}$), which occurs in competition with the back electron transfer ($k_{-1}$). The effective overall rate constant ($k_{EX}$) for the whole electron transfer process, under the consideration of steady-state assumption and equilibrium approximation, is given by:

$$k_{EX} = \frac{k_{1}k_{2}}{k_{2} + k_{-1}}$$

The redistribution of counterions ($k_{2}$) is modeled as diffusion over a distance “a” to relieve the Coulombic imbalance induced by the electron transfer:\textsuperscript{22}

$$k_{2} = D_{CION} \left( \frac{\pi}{2a} \right)^{2}$$

If the counterion diffusion is much faster than the electron transfer reaction ($k_{-1} \ll k_{2}$), $k_{EX}$ should reflect the intrinsic electron transfer dynamics ($k_{1}$). On the other hand, if $k_{-1} \gg k_{2}$, then

$$k_{EX} = \frac{k_{1}}{k_{-1}} k_{2} = K_{eq} k_{2} = K_{eq} D_{CION} \left( \frac{\pi}{2a} \right)^{2}$$
Figure 6.8 (a) Linear log-log relationship between $k_{EX}$ and $D_{ION}$ for Fc$^{+1/0}$ electron transport in undiluted ferrocenated imidazolium ionic liquids over the temperature range of 25°C to 75°C in vacuum. (b) The data in (a) co-plotted with literature data from CO$_2$ plasticized melts, [Co(phen)$_3$](MePEG$_{350}$SO$_3$)$_2$$_{11b}$ (▽) and [Co(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$](ClO$_4$)$_2$$_{11a}$ (▼), MePEG$_{350}$ plasticized melt [Co(phen)$_3$](MePEG$_{350}$SO$_3$)$_2$$_{11c}$ in mole ratio of 6:1 (○), 3:1 (□) and 2:1 (△), and [Co(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$](ClO$_4$)$_2$+xLiClO$_4$$_{6b}$ (■) (x=0~1.31), [Ru(bpy(CH$_2$MePEG$_{350}$)$_2$)$_2$](CN)$_2$ plasticized with CO$_2$ (over a range of temperatures)$_{11d}$ (●), [Ru(bpy(CO$_2$MePEG$_{350}$)$_2$)$_3$][X]$_2$, where X=ClO$_4^-$ or a mixture of ClO$_4^-$ and I$^-$$_{11e}$, [Cp$_2$Co](MePEG$_{350}$SO$_3$) melt (neat, MePEG$_{350}$ plasticized or mixed with [FcTMA]$^+$)$_{10}$ (▲), and Au$_{38}$ nanoparticle polyether molten salts(♦)$_{12}$ The overall slope for the linear correlation is 1.00.
\[
\log(k_{\text{EX/M}-1\text{s}^{-1}})
\]
where $k_{\text{EX}}$ is controlled by the relocation of counterions and reflects the dynamics of counterion diffusion instead of the intrinsic electron transfer reactions. In this case, the value of $k_{\text{EX}}$ reflects the dynamics of counterion motion and of electron transport, not that of the intrinsic electron transfer dynamics.

Log-log plots of $k_{\text{EX}}$ and $D_{\text{CION}}$ obtained for selected ferrocenated imidazolium ionic liquids are shown in Figure 6.8(a). The linear correlation with near unity slope clearly justifies that in the ionic liquid redox system, the counterion diffusion is slow enough (comparing to the intrinsic electron transfer reaction) to be the controlling step in the electron transfer process. What is even more significant is that the transport data from the ferrocenated imidazoliums, when plotted along with the data from various redox molten salts, distribute around the same region and a common fitting line can be drawn as shown in Figure 6.8(b), suggesting a similar mechanism of electron transfer. The intercepts in the plot, according to equation (4), are determined by the values of “$K_{eq}$” and “$a$”. Assuming that $K_{eq}=1$ for symmetric electron self-exchange reaction in all redox molten salts, the rather similar intercept offsets for different redox systems, with different dimensions and concentrations, suggest that the diffusion length “$a$” is not strongly dependent on the average redox center-to-center distance ($\delta$) or redox concentration. Typically, “$a$” is much smaller than the average center-to-center separation. For the ferrocenated imidazoliums shown in Figure 6.8(a), the distance of “$a$” is ca. 2~3 Å, whereas the equilibrium ferrocene-ferocene center-center separation is 8~9 Å. The average “$a$” value derived from the common correlation line in Figure 6.8(b) is 5.1 Å while that of the redox center-to-center distance in metal complex polyethers is 15~17 Å. Clearly, the small difference of offsets in Figure 6.8 should not simply reflect the change of $\delta$ from one redox system to another.
It is also quite possible that the various intercept offsets in the data sets reflect small differences in the electron transfer $K_{eq}$. This may be especially true for one peculiar set of data in Figure 6.8(b), which lies on a correlation line set aside (to the right), namely the $[\text{Ru}(\text{bpy}(\text{CH}_2\text{MePEG}_{350})_2)_2](\text{CN})_2$ melt. The shift of intercept may be attributed to the asymmetric structure of this ruthenium complex which may invoke a relative smaller $K_{eq}$ value than other redox systems. A related discussion is presented elsewhere.\textsuperscript{11d}

Again, the significance of Figure 6.8(b) is that the ionic relaxation model of control of electron transport, which has no assumption regarding the particular nature of redox sites, is quite general for different redox semi-solid systems, from metal complexes\textsuperscript{11}, molecule-like Au nanocrystals\textsuperscript{12} to redox imidazoliums.

### 6.3.5 Sorption of CO$_2$ at High Pressure

The ferrocenated imidazolium ionic liquid with short alkyl chain and ester linkage in the cationic structure is rather rigid and shows limited ionic conductivities due to the limited free volume in the materials.\textsuperscript{13} A few examples of this kind are shown in Table 6.2, where some ILs are so viscous that diffusion coefficient measurements by chronoamperometry is difficult even at elevated temperature.

Nonetheless, the fluidity of imidazolium ILs can be enhanced in high pressure CO$_2$. It is reported that CO$_2$ can easily dissolve into the imidazolium-based ionic liquids where CO$_2$ serves as a reagent for chemical reaction.\textsuperscript{24} From our experience with polyether melts, the sorption of CO$_2$ lowers the viscosity of material and enhances the ionic mobility due to the free volume increase.\textsuperscript{11a,b,12} Here, a similar high-pressure CO$_2$ sorption experiments were carried out for the first time in ferrocenated imidazolium ionic liquids. Figure 6.9 shows the
Figure 6.9. Microelectrode cyclic voltammogram (10 mV/s) of undiluted ferrocenated imidazolium ionic liquids, [Fc-CO2-C3-Im-Me][PF$_6$], at 65°C on 12.5 µm Pt disk electrode in vacuum and different CO$_2$ pressure.
Figure 6.10  Apparent (electron) (●) and ionic physical diffusion coefficient (■) of [Fc-CO2-C3-Im-Me][PF₆] in varied CO₂ pressure at 65°C.
Figure 6.11 Arrhenius plots of apparent (electron) (below) and ionic diffusion coefficients (above) at varied temperatures in different CO2 pressure: 200 psi (●), 400 psi (■), 600 psi (▲), 800 psi (▼), 1000 psi (◆). The thermal barriers of apparent and ionic diffusion are 109, 82, 71, 56, 53 kJ/mol and 109, 80, 56, 35, 31 kJ/mol, respectively.
**Table 6.3** Physical transport and electron-transfer results for [Fe-CO2-C3-Im-Me][PF₆] ionic liquids in high pressure CO₂.
<table>
<thead>
<tr>
<th>Measured parameter / CO₂ pressure (psi)</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{\text{APP}} (65^\circ \text{C}) / 10^{-9} \text{ cm}^2 \text{ s}^{-1}$</td>
<td>0.8</td>
<td>1.4</td>
<td>2.5</td>
<td>3.2</td>
<td>4.2</td>
</tr>
<tr>
<td>$k_{\text{EX}} (65^\circ \text{C}) / 10^5 \text{M}^{-1} \text{ s}^{-1}$</td>
<td>2.3</td>
<td>4.2</td>
<td>7.3</td>
<td>9.6</td>
<td>12</td>
</tr>
<tr>
<td>$E_{\text{A,ET}} / \text{kJ mol}^{-1}$</td>
<td>109</td>
<td>82</td>
<td>71</td>
<td>56</td>
<td>53</td>
</tr>
<tr>
<td>$D_{\text{ION}} (65^\circ \text{C}) / 10^{-10} \text{ cm}^2 \text{ s}^{-1}$</td>
<td>0.3</td>
<td>1.2</td>
<td>2.9</td>
<td>5.5</td>
<td>9.5</td>
</tr>
<tr>
<td>$E_{\text{A,ION}} / \text{kJ mol}^{-1}$</td>
<td>109</td>
<td>80</td>
<td>56</td>
<td>35</td>
<td>31</td>
</tr>
</tbody>
</table>
cyclic voltammetry of [Fc-CO2-C3-Im-Me][PF$_6$] at different CO$_2$ pressure up to 1000 psi. The increased peak current and reduced potential peak spacing at higher CO$_2$ pressure signify enhancement of diffusion coefficients and alleviated $iR_{UNC}$ distortion, respectively. The quantitative measurement of electron and mass transport in [Fc-CO2-C3-Im-Me][PF$_6$] at different CO$_2$ pressure is also achieved with results shown in Figure 6.10 and Table 6.3. Clearly, both apparent diffusion and physical diffusion of ions are enhanced, behaving quite similar to polyether melts, as the CO$_2$ pressure gets higher. The extent of increase tends to level off at higher CO$_2$ pressure presumable due to the saturation of CO$_2$ sorption$^{11a}$ Further increase of CO$_2$ pressure into the supercritical state (T>31$^\circ$C)$^{25}$ or liquid state (T<31$^\circ$C) does not seem to have any further effect.$^{26}$ The increase of both $D_{APP}$ and $D_{ION}$ is also accompanied by a decrease of thermal barriers. As illustrated in Figure 6.11 and Table 6.2, the thermal barriers of both $D_{APP}$ and $D_{ION}$ decrease by 2- to 3-fold at higher CO$_2$ pressure.

In the context of ionic relaxation control of electron transfer discussed above, the thermal barrier of electron transfer should be similar to that of ionic diffusion since the measured electron transfer rate is a reflection of counterion dynamics. The observed thermal barrier of electron transfer is quite similar to that of ionic diffusion at lower CO$_2$ pressure, as what predicted from ionic relaxation model. However, the energy barriers tend to become different at higher CO$_2$ pressure. Interestingly, this discrepancy was also been observed with samples of [Fc-CO2-C11-Im-Bu] where the thermal barrier of $D_{APP}$ is larger than that of $D_{ION}$ as shown in Table 6.2. Given that both [Fc-CO2-C11-Im-Bu] and CO$_2$ swollen [Fc-CO2-C3-Im-Me] have large free volume with improved fluidity, it is possible that there is some energy contribution of physical diffusion of ferrocenated imidazoliums into the electron transport process. However, the Arrhenius plot of $D_{APP}$ does not show the obvious
curvature that would be an indicator of coupled physical transport to the electron transfer process.\textsuperscript{6c, 27} Eventual clarification of this problem would require a probe of redox (e.g. cobaltocenium) imidazolium ionic liquid with the iso-structure to ferrocenated imidazoliums as surrogate to differentiate the physical diffusion from the apparent electron diffusion coefficient.\textsuperscript{11f} More investigation in this direction is undergoing and will follow soon.
REFERENCES AND NOTES


13. See Chapter V.


16. The anodic ($i_{p,a}$) and cathodic peak current ($i_{p,c}$) are used to estimate the maximum $iR$ distortion.


23. The average redox center-to-center distance ($\delta$) is calculated from the molar concentration (C) on the basis of simple cubic lattice model, i.e., $C=1/(\delta N_A)$.


25. The critical pressure of CO$_2$ is 1070 psi and critical temperature is 31°C.

CHAPTER VII

ELECTROCHEMICAL CONTACT ANGLE MEASUREMENT OF IONIC LIQUID ON FILMS OF AU NANOPARTICLES

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7.1 Introduction

The contact angle ($\theta$) of a liquid droplet on a solid surface is defined as the angle formed between contact line of liquid/vapor and liquid/solid and is determined by the interfacial tension as described by Young’s equation.\(^1\) For a given three-phase system at equilibrium, the contact angle is predicted as:

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$$

where $\gamma$ are the interfacial tensions of solid/vapor (SV), solid/liquid (SL), and liquid/vapor (LV), respectively.

There are numerous fluids used in contact angle measurements, including aqueous and aqueous surfactant solution, and various organic solvents.\(^2\) Those fluids have high to moderate vapor pressure at room temperature and evaporate in ambient conditions, requiring control of vapor pressure in a closed chamber.\(^3\) The popular imidazolium- and pyrrolidinium-based room temperature ionic liquids (RTILs) are easier subjects for contact angle
measurement thanks to properties such as negligible vapor pressure, nonflammability, and good chemical and thermal stability. The intrinsic ionic conductivity of RTIL provides further advantage for related electrochemical applications without the requirement of adding supporting electrolyte.¹⁴

The contact angle measurement on the electrode surface as a function of external potential has been a traditionally interesting topic in the areas of electrocapillary theory⁵ and adsorption,⁶ and has recently showed signs of rejuvenation thanks to the recent advancement in electrowetting.⁷ Electrowetting is the phenomenon of contact angle decrease under the influence of an external voltage (1⁰⁻¹⁰² V) applied across the liquid/insulator/electrode interface. Electrowetting offers an interesting possibility to enhance the wettability of hydrophobic materials without altering the chemical composition of the contacting phases, and thus attracts interest in the areas of microfluidics⁸, liquid lens⁹, and electronic paper¹⁰.

Unlike electrowetting where an insulating layer of hydrophobic polymer covers the substrate, we are interested in dynamic contact angle measurements on an electrode substrate coated with films of electroactive substance that exhibits a current-potential wave at electrode potentials characteristic of electrochemical reactions of immobilized redox species. If the surface wetting properties of the film on the electrode are affected by the charge state of the redox film, a dynamic contact angle change should be observable as the electrode potential is swept to different electrochemical charge states of film.³

In this chapter, the surface properties of monolayer-protected Au nanoparticle (Au₁₄₀(C6)₅₃, Au₃₈(PhC₂)₂₄) coatings on electrodes under active potential control are studied based on their contact angle measurement using 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid as the film phase. The Au nanoparticles mentioned here
have core diameter less than 2 nm, a dimension bridging the bulk metal and molecular Au complex, and show molecule-like electrochemical redox behavior. A droplet of ionic liquid is placed on the films of Au nanoparticles that have been dropcast on a solid Au surface that is subsequently placed under active potential control. The ionic liquid droplet also serves as the electrochemical cell in the experiment. Miniature reference and counter electrode are inserted into the top of droplet. The contact angle change is observed with cyclic voltammetric potential function applied between the droplet of ionic liquid and the film of Au nanoparticles coated on the electrode. The potentials applied are much smaller than required for electrowetting effects on insulating hydrophobic polymers. The dynamic contact angle observed typically decreases as the electrode potential is swept through a series of nanoparticle oxidation wave. The change in contact angle is irreversible, that is, it does not reversibly increase during the reverse potential scan. The origin of the contact angle change is discussed on the basis of electrochemically-induced ion partition, with comparison to the phenomenon of electrowetting.

Supporting experiments of measuring ionic liquid contact angles were also done on bare gold electrodes and on electrodes coating with alkanethiolate self-assembled monolayers.

7.2 Experimental

Chemicals. All chemicals are used as received. 1-Butyl-3-methylimidazolium hexafluorophosphate ionic liquid (Fluka, >96%), benzeneethanethiol (Aldrich, 98%), 1-dodecanethiol (Aldrich, 98+%), hexanethiol (Fluka, 95%), ethanol (AAPER, 200 proof), methylene chloride (Fisher, optima).

Treatment of Au Film. A 200 nm thick Au film was formed by evaporation of Au onto a
Figure 7.1 A cartoon of “droplet” electrochemical cell and dynamic contact angle measurement under active potential control. The decrease of contact angle is illustrated by the arrow.
glass substrate, following an adhesion undercoating of a 10 nm thin layer of chromium. The Au film was cleaned by Piranha solution (30 min), followed by sonicating and thorough washing with Nanopure water and 100% ethanol, respectively. The film was dried by high pressure Ar gas flowing out of a syringe and used promptly in the following step.

**Droplet Electrochemistry and Contact Angle Measurement.** The synthesis of Au nanoparticles, Au$_{140}$(C6)$_{53}$ and Au$_{38}$(PhC2)$_{24}$, followed the strategy described before.$^{11}$ The film (ca. 100s µm) of Au nanoparticles was prepared by casting several drops of dilute Au nanoparticle solution (5 mg/mL in CH$_2$Cl$_2$) onto the Au surface on glass and further dried in vacuum for overnight. The nanoparticle coating was roughly 5~10 cm$^2$. A 4 µL drop of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (Fluka, 96%) was placed on the Au nanoparticle film through a 10-µL electronic pipette. Two Pt wires with diameter of 25 µm were inserted into the droplet from the top and connected to the potential stat as reference and counter electrode, respectively. The position of these two electrodes was precisely controlled with a home-made three-way stage. The Au surface underneath the Au nanoparticle film was treated as the working electrode. The contact angles were measured with a Rame-Hart optical goniometer at ambient condition. The electrochemistry and potential function control was conducted with a CH Instruments Electrochemical Workstation. A typical experimental setup is illustrated in Figure 7.1.

**SAM Preparation.** The self-assembled monolayer (SAM) of alkyl- or aromatic-thiol on Au film was prepared by immersing into a dilute ethanol solution of corresponding thiols for two days. The surface was thoroughly washed by ethanol to get rid of unbonded thiol and dried at ambient condition.$^{12}$
7.3 Results and Discussion

7.3.1 Voltammograms of Au Nanoparticle Film Contacted with Ionic Liquid

Before dealing with Au nanoparticles, the cyclic voltammogram (CV) of a film of ferrocene coated on the solid Au electrode surface and contacted with 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid is obtained and shows the characteristic of \( \text{Fc}^{+1/0} \) redox wave, as shown in Figure 7.2. This scenario looks similar to the voltammetric studies of adhered microparticles in contact with bulk ionic liquids by Bond et al.\(^{13}\) It was demonstrated in his study that, in many cases, the voltammogram of redox reaction in the solid phase is indistinguishable from that obtained from the same redox fully dissolved in ionic liquids due to the rapid solvation of electrogenerated redox ions. However, contrary to Bond’s observation, the CV of ferrocene in Figure 7.2 does not show classical behavior associated with the diffusion-controlled process in solution but, instead, shows evidence of surface confinement of the redox species, with peak separation of only 48 mV. This observation is similar to those in Willman’s poly(vinylferrocene) experiments.\(^3\)

One should notice that in Bond’s experiment,\(^{13}\) the ferrocene is attached to the electrode surface by mechanically rubbing over the solids, resulting a porous structure with micro-particles of ferrocene scattered around on the electrode. When in contact with the ionic liquid, the voids between the microparticles of ferrocene and electrode can be filled up. It is probably those contact area, where the ionic liquid, ferrocene solid and electrode meet, that makes solution-like electrochemistry possible. However, the film of ferrocene in our present case is prepared by dropcasting from solution and may have a much more uniform multilayer structure which separates the ionic liquid phase and the electrode. While rapid dissolution of oxidized ferrocene may happen at the interface with the ionic liquid, the
**Figure 7.2** Cyclic voltammogram (10 mV/s) of ferrocene film obtained from the “droplet” electrochemical cell of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid with Au flat working, Pt reference and counter electrode.
[BMIM][PF6]/Fc/Au

Potential (V)

10 \mu A

0.8  0.6  0.4  0.2  0.0

Potential (V)
majority of ferrocene inside the film undergoes electrochemistry characteristic of surface confinement. Given the multi-layer structure of film, the electron transport by hopping reaction over different layers of redox species should be also important for the successful observation of voltammetric signals.

In a similar fashion to the ferrocene film, cyclic voltammograms of a \( \text{Au}_{140}(\text{SC6})_{53} \) film contacted with 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid is obtained as shown in Figure 7.3. As observed before with \( \text{Au}_{140}(\text{SC6})_{53} \) in dilute solution\(^{14,15} \), the voltammogram of \( \text{Au}_{140} \) film shows series of quantized double layer charging peaks with presumably assigned +1 to +4 oxidative state, corresponding to single electron changes in the charge state of Au core\(^{16} \). The peak potentials (both anodic and cathodic) of each charge state, along with the calculated formal potentials, are listed in Table 7.1. The formal potential spacing of any two adjacent charge states, \( \Delta E_{Z+1,Z} \), is described by\(^{14,15} \):

\[
\Delta E_{Z+1,Z} = \frac{e}{C_{DL}}
\]

(2)

where \( C_{DL} \) is the double layer capacitance of single Au nanoparticle and \( e \) is the single electron charge. The values of \( C_{DL} \), determined from the formal potential spacing, are listed in Table 7.1. Clearly, there is an obvious dependence of \( C_{DL} \) on the charge state of \( \text{Au}_{140} \), in contrast with the pattern of more or less evenly spaced current peaks observed in dilute solution\(^{15} \). A simple calculation of average \( C_{DL} \) of \( \text{Au}_{140}(\text{SC6})_{53} \), provided a average formal potential peak spacing of 195 mV, gives a value of 0.82 aF, which is much larger than those obtained in \( \text{CH}_2\text{Cl}_2 \): 0.57 aF for dilute \( \text{Au}_{140}(\text{SC6})_{53}/\text{CH}_2\text{Cl}_2 \) solution\(^{17} \) and 0.75 aF for SAMs of \( \text{Au}_{140} \) on Au electrode in contact with \( \text{CH}_2\text{Cl}_2 \) solution\(^{18} \). According to the concentric sphere capacitance model, the capacitance of monolayer-protected Au nanoparticles can be approximated by\(^{14,19} \).
**Figure 7.3** Cyclic voltammogram (10 mV/s) of \( \text{Au}_{140}(\text{C6})_{53} \) film obtained from the “droplet” electrochemical cell of 4 µL 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid on flat Au working electrode with inserted micro- Pt reference and counter electrodes. The inserted voltammogram shows the potential scan covering negative region (0 V → -0.5 → +1.2 → -0.5 V) and is obtained with a smaller Pt disk electrode (25 µm, dia.) under vacuum to avoid the complication of oxygen reduction.
Table 7.1 Peak potentials from cyclic voltammograms (10 mV/s) of Au$_{140}$(C6)$_{53}$ film coated on the flat Au electrode surface and contacted with 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid. A micro-Pt reference and counter electrode is inserted into the cell from the top.
<table>
<thead>
<tr>
<th>Charge State, z/(z+1)</th>
<th>+1/0</th>
<th>+2/+1</th>
<th>+3/+2</th>
<th>+4/+3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{p,a} / \text{mV} )</td>
<td>381</td>
<td>608</td>
<td>730</td>
<td>853</td>
</tr>
<tr>
<td>( E_{p,c} / \text{mV} )</td>
<td>112</td>
<td>379</td>
<td>659</td>
<td>812</td>
</tr>
<tr>
<td>( \Delta E_p / \text{mV} ) [=E_{p,a}-E_{p,c} ]</td>
<td>269</td>
<td>229</td>
<td>71</td>
<td>41</td>
</tr>
<tr>
<td>( E_z^o / \text{mV} ) [=(E_{p,a}+E_{p,c})/2 ]</td>
<td>247</td>
<td>494</td>
<td>695</td>
<td>833</td>
</tr>
<tr>
<td>( \Delta E_{z+1,z}^o / \text{mV} ) [=E_{z+1}^o-E_z^o ]</td>
<td>247</td>
<td>201</td>
<td>138</td>
<td>----</td>
</tr>
<tr>
<td>( C_{DL}/\text{aF} ) [=e/ \Delta E_{z+1,z}^o ]</td>
<td>0.65</td>
<td>0.80</td>
<td>1.16</td>
<td>----</td>
</tr>
</tbody>
</table>
\[ C_{DL} = 4\pi \varepsilon_0 \varepsilon \frac{r}{d} (r+d) \]  

where \( \varepsilon \) is the dielectric constant of monolayer, \( r \) the radius of core, \( d \) the thickness of monolayer and \( \varepsilon_0 \) the permittivity of free space. The significantly increased double layer capacitance may reflect the change of effective dielectric constant of protecting monolayers on Au nanoparticle since, in one of Chen’s reports, a surface anchored Au_{140}(SC6)_{53} film contacted with H_2O (\( \varepsilon=80 \)) also shows a much larger double layer capacitance of 1.05 aF.\(^{20}\) However, the film studied here is not a SAM as in Chen’s report but, instead, a multi-layer structure which is physically adhered to the electrode surface. Therefore, the observation of double-layer charging peaks in Au nanoparticle film, along with the increased effective dielectric constant, suggests that the positively charged Au_{140} might pair with small size PF_{6} anions which penetrate into the network structure of Au nanoparticles.

Careful examination of data in Table 7.1 leads to more evidence supporting the discussion above. First of all, the potential peak spacing (\( \Delta E_p \)) is getting smaller at more positive charge state, signifying the reduced \( iR_{UNC} \) effect with the increasing amount of ions penetrating into the film. Secondly, the dependence of \( C_{DL} \) on the charge state of Au_{140} (as shown in Table 7.1) suggests that the effective dielectric constant of protecting-monolayer of Au_{140} increases as the Au particles are more highly charged, provided that the monolayer thickness is constant in the solid film.\(^{14,19}\) The change of dielectric constant is likely due to the inclusion of PF_{6}^{−} anions into the otherwise hydrophobic alkyl monolayer of Au_{140} and should depend on the concentration of surrounding anions as a function of charge state of Au_{140}, as observed in dilute solution where \( C_{DL} \) increases with the concentration of supporting electrolyte.\(^{21}\)
One peculiar feature of voltammograms shown in Figure 7.3 is that there is no charging peak recognizable in the negative potential regime, which is in contrast with the series of oxidation peaks in the positive potential region. This “current rectifier” behavior has been observed before on a SAM of Au$_{140}$(SC$_6$)$_{53}$ contacted with H$_2$O.$^{20}$ The quantized double layer charging only appears at positive potential region due to the binding of relatively hydrophobic PF$_6^-$ anions into the monolayer and repulsion of hydrophilic water from interparticle voids, which makes the double layer charging capacitance ($C_{DL}$) of nanoparticles dominate over background electrode double charging ($C_{EL}$). The situation in the present case is somewhat similar, but without the complication of water. The appearance of quantized double layer charging peaks at positive potential is driven by the coupling of small size PF$_6^-$ anions with positively charged Au nanoparticles. The penetration of PF$_6^-$ ions into the monolayer of Au nanoparticle increases the effective dielectric constant and therefore results a larger $C_{DL}$ than $C_{EL}$. However, when the potential is scanned to negative potentials, there is no quantized double layer charging current observed. Given the large size of imidazolium cations, it is likely that electrostatic ion pairing force between negatively charged Au$_{140}$ and imidazolium is small. The difficulties of penetration of imidazolium cations into the monolayer of Au nanoparticles, along with the repulsion of PF$_6^-$ anions, may result a much smaller $C_{DL}$ than $C_{EL}$. Essentially the film works as an insulating layer and the observed current is mainly contributed by the background capacitive charging on both sides of film. It is also seems that the partition of PF$_6^-$ anions into the film is a rather irreversible process since, as shown in Figure 7.3, the background current does not decay entirely to the initial value when the potential scans back to negative region again. The resulting background capacitive current is much larger than that during the initial potential scan from zero to negative region.
Figure 7.4 Cyclic voltammogram (10 mV/s) of Au$_{38}$(PhC$_2$)$_{24}$ film obtained from the “droplet” electrochemical cell of 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid with Au flat working, Pt reference and counter electrode. The inserted graph shows the voltammogram obtained on naked Au surface with same volume of droplet.
$[\text{BMIM}][\text{PF}_6]/\text{Au}_{38}(\text{PhC}_2)_{24}/\text{Au}$

Potential (V)

20 nA

| 1.4 | 1.2 | 1.0 | 0.8 | 0.6 | 0.4 | 0.2 | 0.0 |

2 μA

$[\text{BMIM}][\text{PF}_6]/\text{Au}$
Since the existence of PF$_6$ anions effectively increases the dielectric constant of film and therefore corresponding capacitance, the current difference suggests that the repulsion of PF$_6$ out of Au$_{140}$ monolayer is a really slow process.$^3$

Different from Au$_{140}$(SC$_6$)$_{53}$, the voltammogram of Au$_{38}$(PhC2)$_{24}$ film contacted with ionic liquid is featureless, even at the positive potential region, as illustrated in Figure 7.4. The current scale, when compared to the voltammogram obtained from naked Au surface, is several orders of magnitude smaller, demonstrating, in essence, the film of Au$_{38}$(PhC2)$_{24}$ works an insulator layer. It is likely, but may require more evidence, that the aromatic structure of benzeneethanethiol blocks the penetration of ions into the network of multi-layer Au nanoparticles. Another important aspect of Au$_{38}$, which is different from Au$_{140}$, lies in the evolution of large HOMO-LUMO (highest occupied molecular orbit-lower unoccupied molecular orbit) electronic energy gap due to its smaller core size.$^{22}$ For example, the cyclic voltammogram of Au$_{38}$(PhC2)$_{24}$ shows a 1.6 V separation between the first oxidation and reduction peak, which is much larger than the corresponding peak spacing (~280 mV) of Au$_{140}$(C$_6$)$_{53}$.$^{14, 15}$ Therefore, the population of thermally-activated charge carriers formed by disproportionation reaction (2Au$_{38}^0$→Au$_{38}^+Au_{38}^-$) in the film of Au$_{38}$ is rather limited.$^{23}$ Since the electron transport from the electrode surface to the interface between solid nanoparticle film and ionic liquid relies on the electron transfer between Au nanoparticles with different charge state, lack of charge carrier in the film leads to much smaller electronic conductivity.$^{24}$ In another word, the film behaves more like an insulator.

### 7.3.2 Static Contact Angle Measurement
The static contact angles of ILs on the Au nanoparticle films are first measured without external potential control. The results are listed along the contact angles of pure water obtained from comparable surfaces in Table 7.2. Preliminary contact angle measurements with different volume of droplet from 1µL to 6 µL were made and the results do not show obvious dependence on the liquid drop size. The 4 µL was chosen due to its appropriate size in the viewfinder of Rame-Hart optical goniometer. For each surface, the contact angle measurements are made repeatedly (8 times) on at least three different spots and the result shown in Table 7.2 is the averaged number. The time dependence of contact angle is also examined. For ILs, the contact angle is steady for hours (the time scale for a full experiment) and it seems that the effect of moisture absorption by the IL is minimal.25 The contact angle measurement of H$_2$O is always carried out immediately after the droplet is placed to reduce the effect of evaporation.

Contact angles of water on the surface of Au nanoparticles coated with dodecanethiolate ligands have been measured before.26 It was found that the contact angles on Au nanoparticles are smaller than those on 2D-SAM of dodecanethiols, perhaps due to the higher surface curvature, which provokes enhanced surface exposure of methylene chain segments. The water contact angle on a surface that exposes mostly methylene groups is usually ~10° smaller than that for a surface of methyl group.27 The same trend is observed here with Au$_{140}$(C6)$_{53}$ films on which the water contact angle (88.8°) is indeed ca. 10° smaller than on the surface of methyl group formed by a SAM of dodecanethiols (97.3°). Also, the water contact angle on Au$_{140}$ is fairly consistent with the previous results of 90.8° to 95.3° for Au nanoparticles with dodecanethiolate monolayers and core diameter from 1.5 to 5.2 nm.26
Table 7.2 Contact angle measurements of pure water and 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid on different surfaces with and without the potential control.
<table>
<thead>
<tr>
<th></th>
<th>angle, deg</th>
<th></th>
<th>angle, deg</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>static(^a)</td>
<td>[BMIM][PF(_6)]</td>
<td>static</td>
<td>dynamic(^b)</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>4.2 ± 0.3</td>
<td>Glass</td>
<td>47.2 ± 1.0</td>
<td>----</td>
</tr>
<tr>
<td>Glass</td>
<td>67.2 ± 2.2</td>
<td>Au</td>
<td>53.3 ± 2.3</td>
<td>53(^c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fc/Au</td>
<td>51.0 ± 1.0</td>
<td>44.8 ± 1.4</td>
</tr>
<tr>
<td>Au(<em>{140})(C6)(</em>{53})/Au</td>
<td>88.8 ± 1.9</td>
<td>Au(<em>{140})(C6)(</em>{53})/Au</td>
<td>64.9 ± 1.3</td>
<td>58.2 ± 1.1</td>
</tr>
<tr>
<td>Au(<em>{38})(PhC2)(</em>{24})/Au</td>
<td>63.6 ± 0.5</td>
<td></td>
<td>64(^c)</td>
<td></td>
</tr>
<tr>
<td>C6(^d) SAM/Au</td>
<td>59.2 ± 1.8</td>
<td>C12 SAM/Au</td>
<td>80.8 ± 1.4</td>
<td>63.6 ± 1.5</td>
</tr>
<tr>
<td>C12 SAM/Au</td>
<td>97.3 ± 0.2</td>
<td>PhC2(^e) SAM/Au</td>
<td>61.0 ± 0.5</td>
<td>52.8 ± 0.6</td>
</tr>
<tr>
<td>PhC2 SAM/Au</td>
<td>80.8 ± 0.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The contact angle without potential control; \(^b\) The minimum contact angle observed (corresponding to maximum contact angle change) with the potential scans to positive potential region (<1.5 V, PtQRE); \(^c\) The height of droplet, an indication of contact angle change, remains the same independent of potential applied. \(^d\) hexane thiol; \(^e\) benzeneethanthiol.
The contact angle of ILs on different surfaces shows that ILs have the lowest surface tension on glass and the largest on the SAM formed by 1-dodecanethiol. Given the polarity difference between these two surfaces, it seems that the trend agrees with general belief that ILs are polar solvents due to their intrinsic high charge density. However, a comparison of contact angle between H2O and ILs shows that the BMIM ILs are much less polar than water and show some relatively hydrophobic properties. From Table 7.2, the IL has a larger contact angle than water on the hydrophilic surface (glass) but smaller contact angles than water on the hydrophobic surfaces of SAM formed by alkyl or aromatic thiols. The alkyl groups in the molecular structure of ILs may contribute to van der Waals interactions with the non-polar hydrophobic surface.

Table 7.2 also shows that the ionic liquid contact angles on films of both Au140(C6)53 and Au38(PhC2)24 are smaller than on the SAM of dodecanethiols, presumably methyl group surface. This result, along with the water contact angle measurements, confirms that the surface properties of Au nanoparticles are closer to those of methylene groups. The comparison is not made with the SAMs of either hexanethiol or benzeneethanethiol, however. Clearly, the quality of those SAMs is far from ideal and the actual surface involves the exposure of mixture of methyl, methylene and phenyl groups.

7.3.3 Electrochemically Induced Contact Angle Change

The dynamic contact angle measurement requires active potential control of Au surface underneath the Au nanoparticle film by the three-electrode potentiostat. The droplet of IL serves an unwalled electrochemical cell with two microelectrodes (Pt wire, 25 µm dia.) inserted from the top as reference and auxiliary electrode, respectively. The insertion of
electrode wires is carried out at the top with care and has no noticeable effect (at least not exceeding the random errors) on the contact angle. The height of droplet, as an indication of contact angle change, is monitored when the cyclic voltammetric potential function is applied. The resulting voltammograms on different films of Au nanoparticles have been discussed as above. The concurrent change of contact angles is shown in Table 7.2.

On the film of Au140(C6)53, the contact angle of ionic liquid is lowered when the potential is scanned to positive region where Au140 is oxidized. Since the contact angle of IL/Au interface does not noticeably depend on the potential (at least in the potential range of interest) as shown in Table 7.2, the reduced contact angle between IL and Au nanoparticle should be solely contributed by the changes in the wetting properties of the nanoparticle interface. Experiments in which potential is stepped incrementally from 0 V toward positive potential show that no obvious change of contact angle occurs until the potential reaches the first oxidation wave, where holding the potential for a sufficiently long time (1000 sec) leads to decrease of contact angle from 64.9° to 58.2°. There is no further change of contact angle observed even the potential is stepped further to the region where Au140 is oxidized to +2, +3, ..., +5. Similar phenomenon is also observed with the Fc film where the decrease of contact angle only starts to happen when the electrode potential attains that for Fc+1/0 oxidation reaction. Holding the potential at the oxidized Fc region for a sufficiently long time eventually gives a contact angle of 44.8°. It should be noted that Willman did similar experiments with H2O (containing 0.1 M KCl) droplet on the polymerized vinylferrocene. In his case, the contact angle also decreased as the Fc was either electrochemically or chemically oxidized. The decrease of contact angle can be easily understood as a result of the reduction of interfacial tension according to Young’s equation. Since the oxidation of
Au$_{140}$(C$_6$)$_{53}$ is accompanied by the dissolution of PF$_6$ anions into the film as discussed above with the voltammetry, the reduced surface tension between IL and Au$_{140}$ film is likely due to the partial swelling of the solid, oxidized film surface regions by PF$_6^-$ penetration.

The change of contact angle in response to the external electric potential is formally similar to the electrowetting, a well-known electrocapillary effect widely used in the applications of microfluidic devices.$^7$-$^10$ In a typical setup of electrowetting experiment, a liquid droplet is placed on the top of a solid electrode (e.g., Au) with a thin layer of hydrophobic material insulating between the liquid and electrode.$^28$ The external voltage applied ($10^0$–$10^2$ V) creates an electric field which drives the oppositely charged species (ions or particles) to the insulator/liquid interface and effectively reduces the interfacial surface tension in accordance with Lippmann’s equation:$^{29}$

$$\sigma = -\left(\frac{\partial \gamma_{SL}}{\partial V}\right)_{p, T, \mu}$$  \hfill (4)

where $\sigma$ is the surface excess charge, $V$ is the external potential applied and the temperature ($T$), pressure ($p$) and chemical composition ($\mu$) held constant. Thanks to the insulator layer between electrical conducting liquid and electrode, the electrowetting is also a capacitance effect where the surface excess charge is linearly correlated to the external potential:$^7f,^{28,30}$

$$\sigma = C \cdot V$$  \hfill (5)

Combination of (1), (3), and (4) gives an equation well-recognized in electrowetting as:$^{7f,28,30}$

$$\cos \theta = \cos \theta_0 + \frac{1}{2\gamma}CV^2$$  \hfill (6)

where $\theta_0$ the contact angle without applied voltage.

Despite the formal similarities, the contact angle change induced by the electrochemical reaction is fundamentally different from the electrowetting effect in that the
Figure 7.5 Comparison of electronwetting with electrochemical reaction induced contact angle change.
effect is driven by a chemical composition change of substrate as a result of electrochemical reaction. In our case, the partition of PF6 anions into the organic component of film induced by the electrochemical oxidation of Au140(C6)53 changes the chemical composition of solid film. The swollen film becomes more or less like the ionic nature of liquid layer, resulting in reduced interfacial tension. The external potential required for electrochemically contact angle measurement is less than 2 V, which is sufficient for electrochemical reaction but much smaller than that in electrowetting for a comparable contact angle change.30 According to equation (4), a large potential is employed in electrowetting due to the low dielectric constant of insulating layer and corresponding relatively small capacitance. Despite the low dielectric constant of monolayer of Au140(C6)53, the electrochemically-induced doping of anions into the film excludes the requirement of large external potential and is essential for the successful observation of contact angle change. A comparison of these two situations is shown in Figure 7.5.

The point above, if correct, suggests that there should be no change of contact angle if the film composition is unaltered during the voltammetric potential scan. Indeed, the contact angle measurement on a film of Au38(PhC2)24 provides a good supporting example. The voltammogram, as shown in Figure 7.4, is almost featureless, demonstrating the sluggish electrochemical oxidation reaction in Au38(PhC2)24 film and slow kinetics of ion penetration. The corresponding contact angle measurement shows no obvious change of contact angle. The result is not surprising since the chemical composition of film remains unchanged independent of potential applied and the film of Au38 is essentially a layer of insulator which would undergo electrowetting with a substantial large external potential applied (~10^2 V).
Lastly, let us consider the hysteresis phenomenon. It is observed that during the dynamic contact angle measurement of Au$_{140}$(C$_6$)$_{53}$ and Fc film, when the potential is scanned in the reverse direction, the contact angle does not retreat back to the initial value even if the potential is held at 0 V for a fairly long time (1 hour). This irreversible change of contact angle was observed previously by Willman et al. and could be explained as the irreversible characteristic of ion embedding into the film.\textsuperscript{3} Retreat of contact angle to initial value requires removing the ions out of a film freshly reduced, which is probably a rather kinetic slow process. As a contrast, the phenomenon of hysteresis is not significant in electrowetting. As a matter of fact, it is the reversibility of electrowetting as a function of potential that makes the “walking” of droplet possible with controlled external potential function.\textsuperscript{7-10,32}
References and Notes


5. Frumkin; Gorodetzkaya; Kabanov; Nekrosov *Phys. Z. Soviet* 1932, 1, 225.


16. The much larger current of the fifth peak in voltammogram, compared to those of the first three peaks, suggest a multi-electron transfer process. Therefore, the fifth peak is not assigned to +5 charge state.


25. The ionic liquid may have been pre-saturated with the air when received. No further purification is conducted since all contact angle measurements are in ambient conditions without special control of humidity.


31. The dielectric constant of hexane is 2.02.

32. See videos at: [http://www.ee.duke.edu/research/microfluidics/](http://www.ee.duke.edu/research/microfluidics/)